REARRANGEMENTS OF BICYCLIC MONOTERPENES

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CONTENTS

ABSTRACT

The stereochemistry of reaction of phenylmagnesium bromide with camphor (43) has been determined. The attempted preparation of the phenyl alcohol (46) by oxymercuration of 2-phenylbornylene (72) resulted in the formation of the vinyl-mercury (81). Consequently the oxymercuration of a number of olefins was carried out to determine the vital structural features for the occurrence of vinylmercury compound formation.

Attempted preparation of epoxides (49 and 50) by m-chloroperbenzoic acid oxidation of the olefin (72) gave largely 2-endo-phenyl ketone (87). An attempt to prepare the bromohydrin (90) by reaction with aqueous N-bromosuccinimide resulted in formation of the bromo-olefin (70). The exo- and endo-epoxides (49 and 50) were prepared by a novel syn-elimination reaction of the two cis-diol monotosylates (60 and 93). The acid catalysed rearrangement of the endo-epoxide (50) gave only the 2-endo-phenyl ketone (87), while the exo-epoxide (49) gave mainly the aldehyde (119).

The cyclic sulphites (95a and 95b) were prepared from the cis-exo-diol (59) obtained by potassium permanganate oxidation of the olefin (72). Thermal rearrangement of the cyclic sulphites gave the aldehyde (119) and the 2-endo-phenyl ketone (87). The greater proportion of the ketone (87) from the anti-cyclic sulphite (95a) has been rationalised in terms of the stereochemistry about the sulphur atom.

A study of the thermal rearrangements of the 2,3-butane epoxides (108 and 109) with sulphur dioxide and the cyclic sulphites (116 and 117) is described.

INTRODUCTION

Rearrangements[1] involve the migration of a group R from the origin, atom A, to a terminus, atom C (Fig.1.).

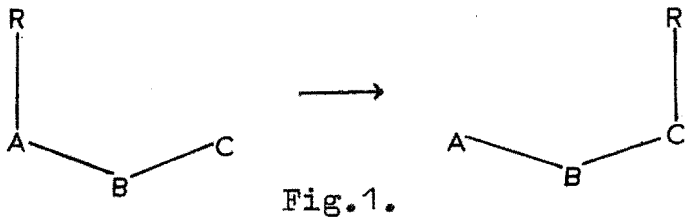


Fig.1.

If a migrating group is transferred from one molecule to another the rearrangement is termed intermolecular, while if the group is transferred to a site within the same molecule the rearrangement is termed intramolecular. A migrating group, transferring with its pair of bonding electons is termed an anionotropic rearrangement, with one of its bonding electrons a free radical rearrangement and with no bonding electrons a cationotropic rearrangement. In the case where the group is a hydrogen atom the anionotropic rearrangement is referred to as a hydride shift, while a hydrogen migration for a cationotropic rearrangement is referred to as a prototropic rearrangement.

Anionotropic Rearrangements

Two early examples of intramolecular 1,2-alkyl shifts were the rearrangement of camphene hydrochloride (5) to isobornyl chloride (1)[2] (Fig.2a.) and the rearrangement of pinacol to

pinacolone[3] (Fig.2b.). Both of these rearrangements are initiated by the formation of a carbonium ion.

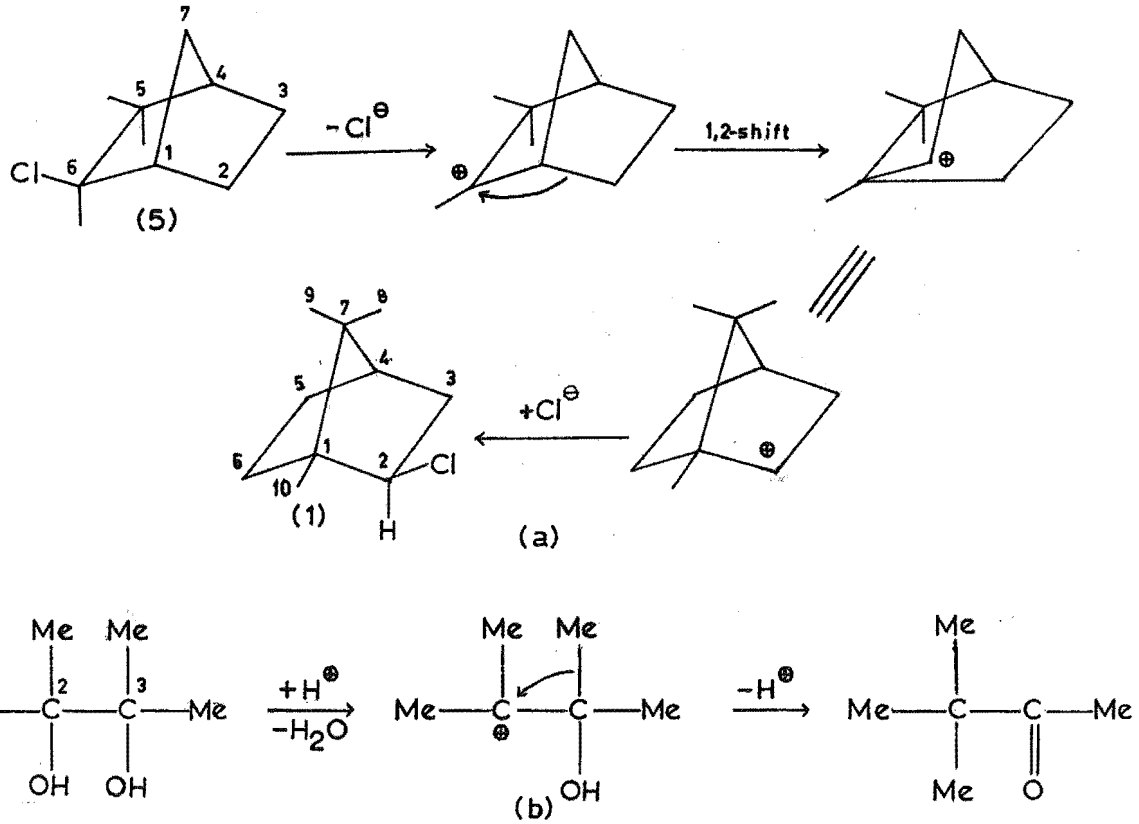


Fig.2.

A rearrangement may involve a sequence of 1,2-shifts as in the "backbone rearrangement" of 3β-friedelanol (2)[4] (Fig.3.).

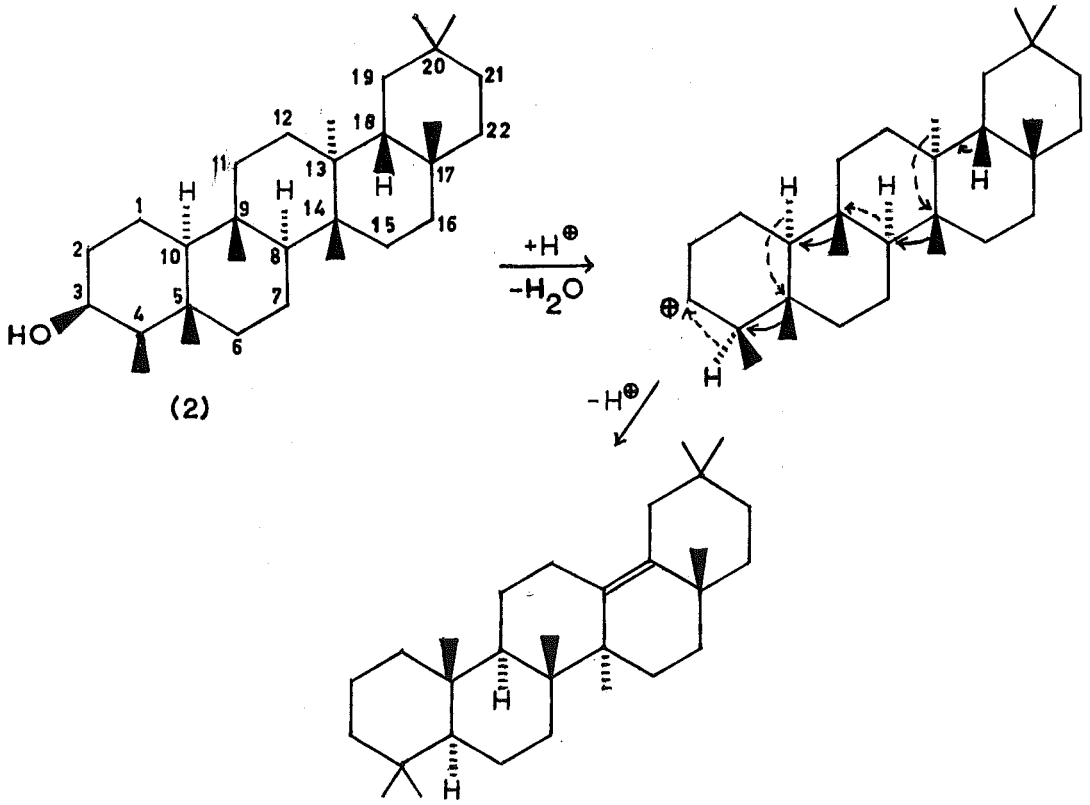


Fig.3.

Carbonium Ion Rearrangements in Bicyclo[2.2.1]heptanes

There are four main types of anionotropic rearrangements common to bicyclo[2.2.1]heptanes:

(a). Wagner-Meerwein rearrangement which involves a skeletal 1,2-shift (Fig.4a.);

(b). Nametkin rearrangement which involves a substituent alkyl 1,2-shift (Fig.4b.);

(c). A 6,1(2)-hydride migration† which involves a 1,3-hydride shift or two 1,2-hydride shifts (Fig.4c.);

(d). A 3,2-hydride migration† which involves a 1,2-

hydride shift (Fig.4d).

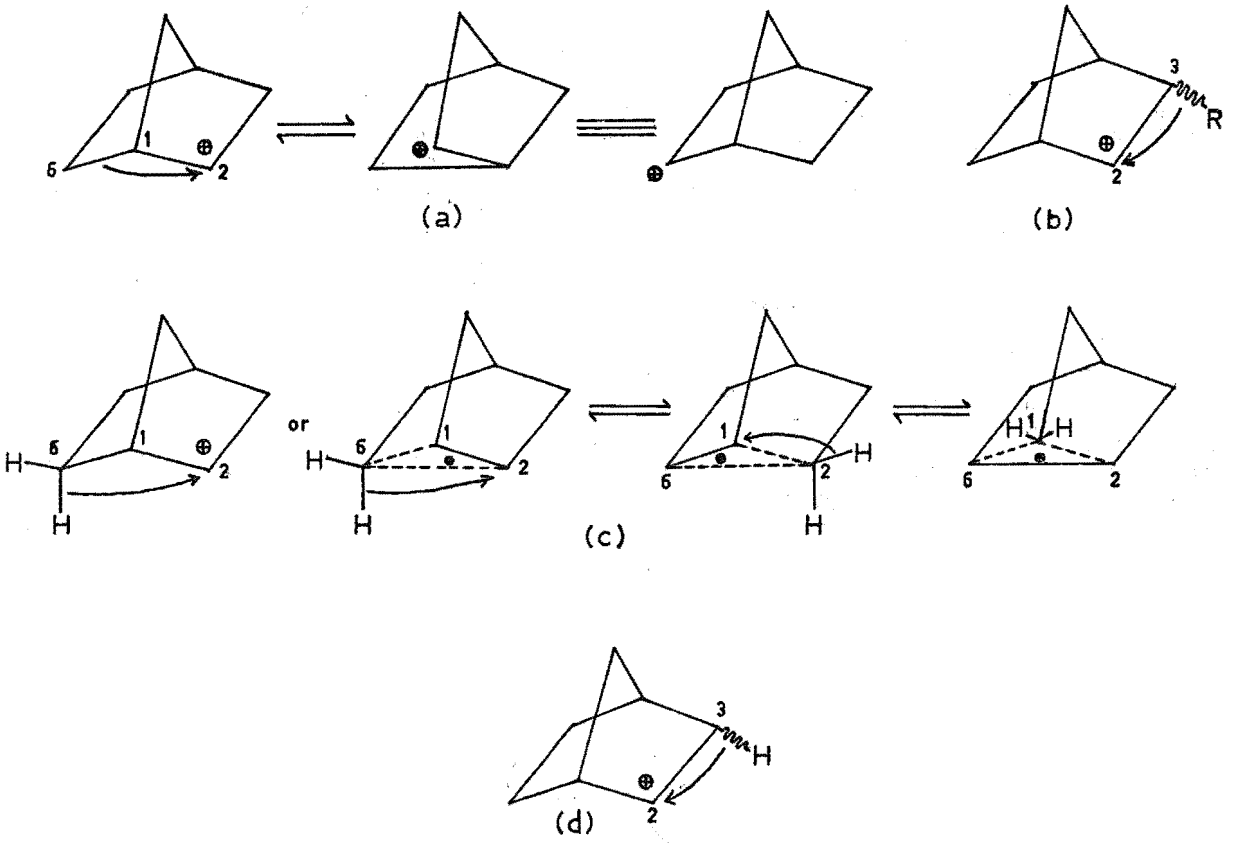


Fig.4.

The Wagner-Meerwein Rearrangement

Reaction of the C^2 carbonium ion with a nucleophile under kinetic control usually results in exo-substitution. It is not possible to explain the greater stereospecificity of this reaction in terms of steric approach control. Nevell et al[4]

†The 6,1(2)-hydride migration and the 3,2-hydride migration nomenclature refers to the carbon atoms involved in contrast to the term 1,2-hydride shift which indicates that the hydride shift involves a migration from one atom to its neighbour.

postulated a "non-classical" or "mesomeric cation" (Fig.5.) to explain the predominance of exo-attack.

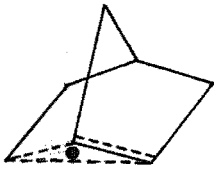


Fig.5.

It is interesting to note that acetolysis of the brosylates (3) and (4) under kinetic controlled conditions[5] give rise to identical product ratios (Fig.6.).

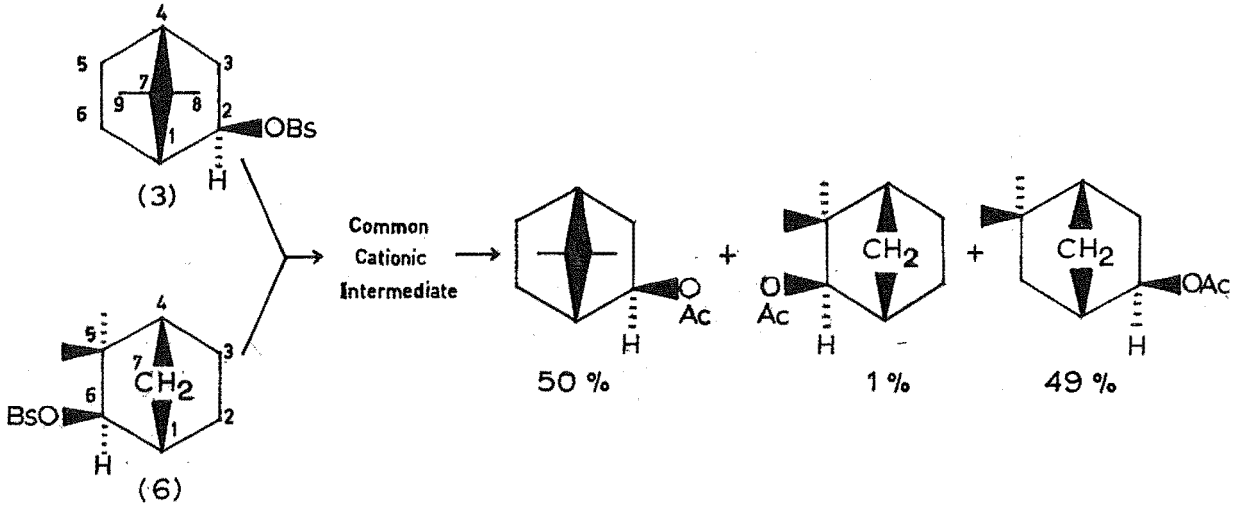


Fig.6.

This has been regarded as evidence in support of a "non-classical" carbonium ion[5].

An alternative explanation involves a rapidly equilibrating classical carbonium ion giving a "windshield wiper effect"[6]. This appears unlikely since this could not explain the exceedingly more rapid rate of solvolysis of an exo-compound cf. an

endo-compound[7]. Solvolysis of optically active exo-norbornyl brosylate (6) gave an exo-product containing <0.02% of the endo-product, the exo-product being > 99.5% racemic[8]. For this to involve two classical carbonium ions would infer a zero $\Delta G^{\neq}$[9]. This is therefore only consistent with the non-classical carbonium ion. The "windshield wiper effect" would also destabilize the classical carbonium ions by allowing decreased endo-face solvation[9].

Certain systems such as nitrous acid on exo- and endo-norbornylamines (8) and (9) give rise to "hot" carbonium ions. In this case the reaction becomes less stereospecific[10,11]. The solvolysis of 1-(p-anisyl) camphene hydrochloride (10) in the presence of $NaBH_4$[12] gives a 13:1 ratio of exo- and endo-products. The predominance of the exo-product in this case should not be explained in terms of a non-classical ion. Schleyer[13] has suggested that torsional effects can account for the stereospecificity involved in these reactions. For example deuteration of camphor at the exo-position[14] will involve a transition state where minimum torsional strain is involved (Fig.7a.) whereas endo-deuteration would involve considerable torsional strain (Fig.7b.).

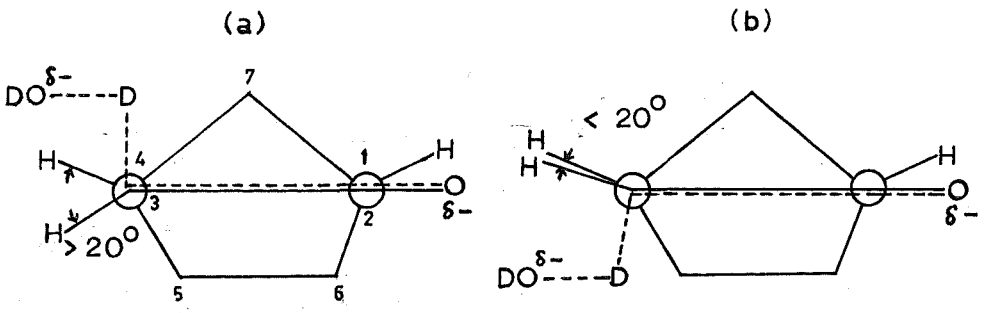


Fig.7.

This effect can also explain the preference for exo-products in all cases where the involvement of the non-classical carbonium ion has previously been proposed.

Olah[15] has examined a number of carbonium ion systems generated by the action of SbF_5-SO_2 on 2-exo-norbornyl chloride (7) using ^1H NMR, ^{13}C NMR and laser Raman spectroscopy. Examination of the norbornyl cation (11) by ^1H NMR at -130° to -154° has indicated a "corner protonated tricyclene" (Fig.8.).

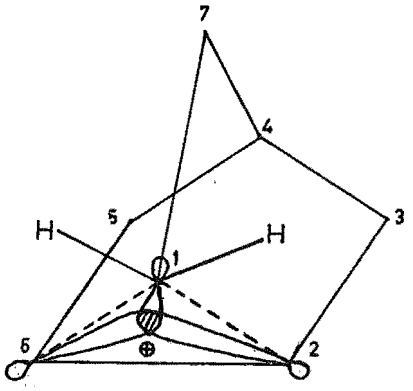


Fig.8.

In the ^1H NMR at -150° where all hydride shifts are frozen out the C^2H is deshielded with respect to the C^1H implying that the C^2 bears a greater degree of positive charge than C^1 (Table.1.).

Table.1.

^1H and ^{13}C NMR Spectra of the Norbornyl Cation (11) at -150°

	^1H NMR			^{13}C NMR	
Proton	δ ppm from TMS	No of protons	Carbon	δ ppm from CS_2	No of carbons
C^1H	3.05	2	C^1	+173	1
C^2H	6.59	2	C^2	+ 70	2

The ^{1}H chemical shifts of the norbornyl cation (11) compared with model classical carbonium ions also supports the non-classical ion structure. The ^{13}C NMR at -150° shows C^{2} is shielded with respect to C^{1} consistent with C^{2} bearing the majority of the positive charge. The ^{1}H and ^{13}C NMR spectra of the norbornyl cation (11) also closely resemble the ^{1}H and ^{13}C NMR spectra of the 7-norbornenyl and 7-norbornadienyl cations (12) and (13) where the positive charge is mainly located on the cyclopropane-type carbon atoms rather than the bridging carbon atom. The laser Raman spectrum for the norbornyl cation (11) has indicated a symmetry analogous to nortricyclene.

A similar study of the 2-methyl- and 2-phenyl substituted norbornyl cations (14) and (15) suggests that 14 is partially non-classical (Table.2.) and 15 is classical. The ^{1}H NMR spectrum of 15 indicates π-delocalization of the phenyl.

In the 2-methylnorbornyl cation (14) the C^{6}-exo-H is deshielded relative to the C^{6}-endo-H indicative of the back lobe of the C^{3}-exo-H orbital tending to overlap with the developing p-orbital as the C^{2}-X bond ionization takes place (Fig.9.).

Table.2.

^{1}H and ^{13}C NMR Spectra of Methyl and Phenyl Substituted Norbornyl (14 and 15) and Cyclopropenyl (16 and 17) Cations

Cation [°C]	^{1}H NMR		^{13}C NMR	
	Proton	δ ppm from TMS	Carbon	δ ppm from CS_2
2-Methylnorbornyl cation (14) [-80°]	C^{6}-exo-H	3.28	C^{1}	+118.0
	C^{6}-endo-H	1.09	C^{2}	-76.1
	$C^{4}H$	2.70		
2-Phenylnorbornyl cation (15) [-35°]	C^{6}-exo-H	2.81	C^{1}	+130.8
	C^{6}-endo-H	2.00	C^{2}	-65.8
	$C^{4}H$	3.20		
1-Methylcyclopropenyl cation (16) [-60°]	———	——	C^{1}	-142.2
1-Phenylcyclopropenyl cation (17) [-20°]	———	——	C^{1}	-70±2

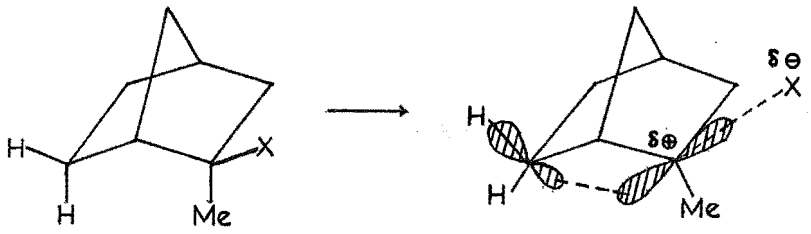


Fig.9.

Presumably the formation of the norbornyl cation (11) involves a similar transition state providing a low energy

route to ionization. If the ^{13}C NMR shift is assumed to vary in a linear manner with respect to charge then the degree of σ-delocalization for the 2-methylnorbornyl cation (14) is ca. 30%.

Thus the norbornyl cation (11) is non-classical in non-nucleophilic solvents at low temperatures. This need not be the case at room temperature in solvolytic conditions.

6,1(2)-Hydride Migration

Dehydration of O-deuterofenchol (18) to give α-, β-, γ- and cyclo- fenchenes (19), (20), (21) and (22) with deuterated potassium bisulphate[16] demonstrates that rearrangement to 20 and 21 involves a 6,1(2)-hydride migration. This rearrangement could proceed via a "face protonated"[17] (Fig.10a.) or "edge protonated"[18] (Fig.10b.) cyclopropane transition state.

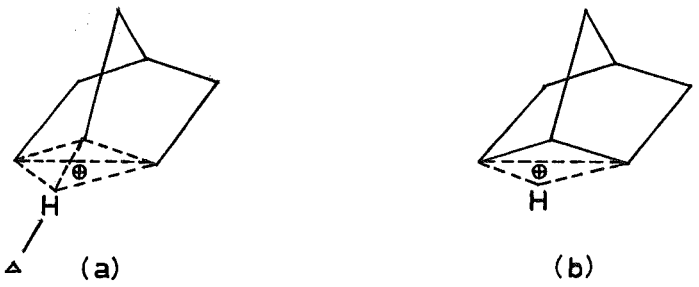


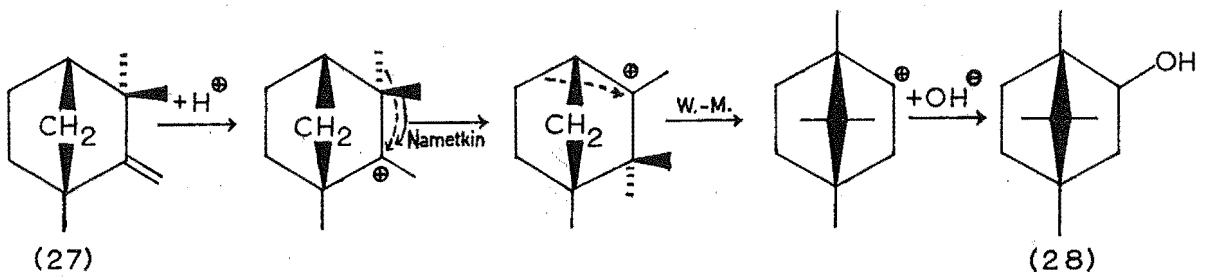
Fig.10.

Winstein[18] has suggested that the 6,1(2)-hydride migration occurs via the "edge-protonated" transition state. Evidence for this "edge-protonated" cyclopropane transition state follows from the acid catalysed rearrangement of the carboxylic acids

(23) and (24) to give the lactones (25) and (26)[19] which result from exclusive endo- to endo- deuteride and hydride migrations. If the rearrangement proceeded via the "face-protonated" transition state involving a symmetrical system with a three-fold axis of rotation for the norbornane skeleton, then the hydrogen and deuterium atoms should show no preference for exo- or endo-attack at the migration terminus.

The Nametkin Rearrangement

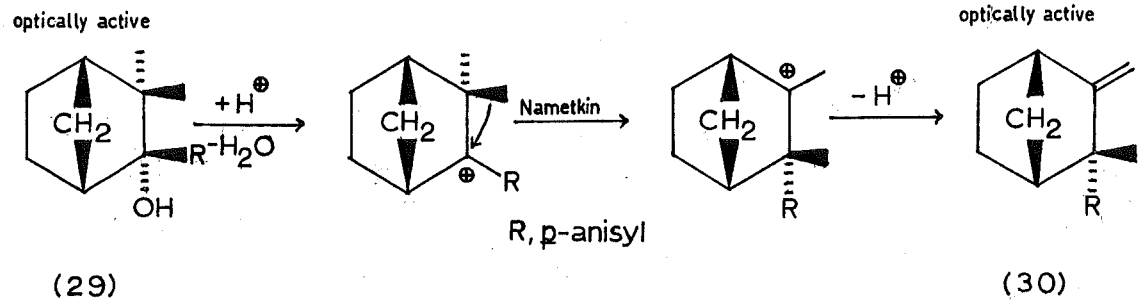
The acid catalysed rearrangement of 1-methylcamphene (27) to 4-methylisoborneol (28)[20] (Fig.11.) is an example of the Nametkin rearrangement.



(27) (28)

Fig.11.

Exclusive exo-alkyl migration occurs as demonstrated for the rearrangement of p-anisyl camphenilol (29) to give olefin (30) by exo-methyl migration[21,22] (Fig.12.).



(29) (30)

Fig.12.

No appreciable p-anisyl shift occurs via an endo-3,2-migration which would give rise to the enantiomer (31).

3,2-Hydride Migration

Evidence for the 3,2-hydride migration comes from the formolysis of exo- and endo-2,3-^{14}C-norbornyl brosylates (32) and (33)[17,23]. Berson et al[24] has shown that acetolysis of the 3-exo-methyl-2-endo-norbornyl brosylate (34) gives 3.5% of the optically active 2-exo-acetoxy-2-endo-methyl norbonane (35) via two Wagner-Meerwein rearrangements, a 6,1(2)-hydride migration and a 3,2-exo-hydride migration. The preference for exo-3,2-hydride migration in this case is explained by intervention of a non-classical carbonium ion. The acid catalysed rearrangement of 2-phenylnorbornan-2,3-cis-exo-diol (36)[25] also gives the product of exo-3,2-hydride migration (37) (Fig.13.) which can be explained by consideration of torsional effects.

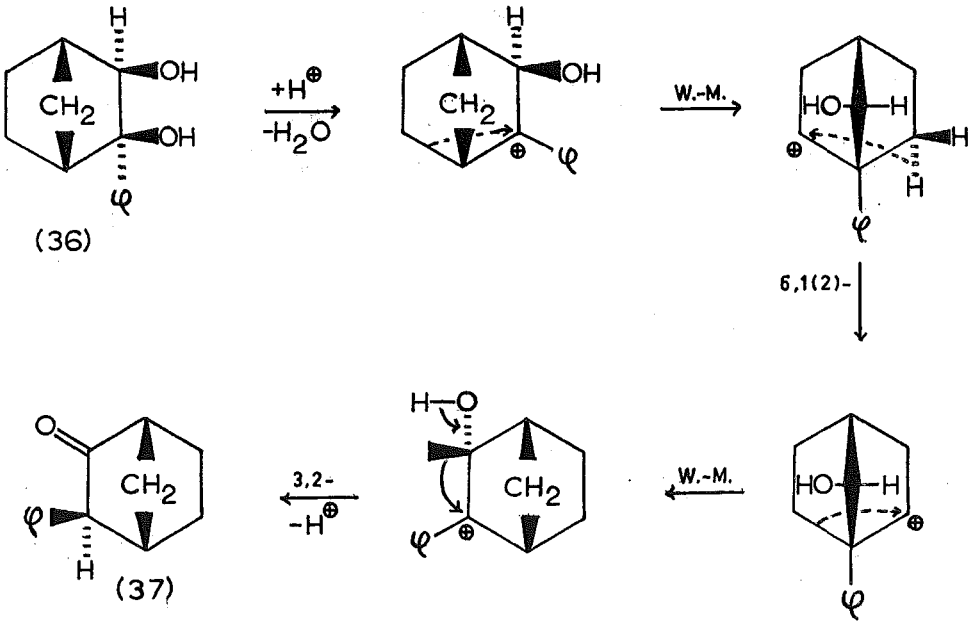


Fig.13.

Rearrangements of 2,3-Oxygenated pinanes

Dansted et al[26,27] found that the products from thermal rearrangement of the 10β-pinane-2,3α-diol cyclic sulphite (38a and 38b) were markedly different from the sulphur dioxide or Lewis acid catalysed rearrangement of the α-pinene oxide (10β-pinan-2,3-epoxide) (39). Pyrolysis of the cyclic sulphites (38a and 38b; 1:1) gave mainly pinocamphone (40; 98%) whereas $MgCl_2$ catalysed rearrangement of the epoxide (39)[28] gave only a trace of pinocamphone (40; 2%) among a series of skeletal rearrangement products. The differing product composition of these reactions both of which proceed via a C^2 carbonium ion (41a and 41b) was attributed to the differing

conformational constraints of the different systems. In the Lewis acid catalysed rearrangement of α-pinene oxide (39) for maximum residual overlap between the departing oxygen and the developing p orbital a conformation is adopted with C^3-H at right angles to the carbonium ion in an unfavourable position for its migration (Fig.14.).

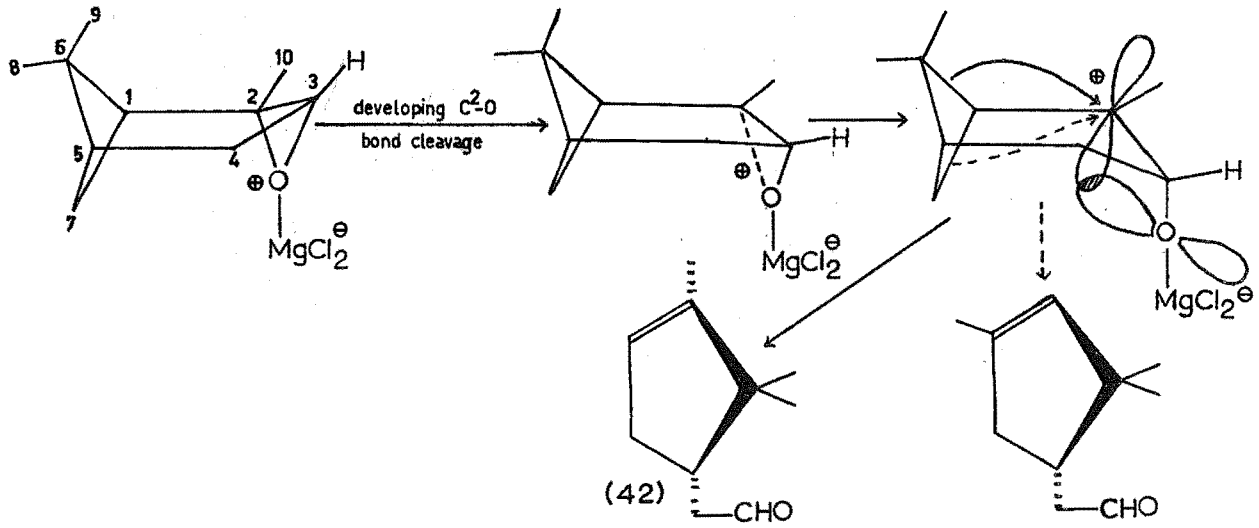


Fig. 14.

The major product the aldehyde (42) results from the more favourable C^1-C^6 migration.

The thermal rearrangement of the more flexible cyclic sulphite (38) proceeds <u>via</u> cleavage of the C^2-O. As a consequence of the more flexible system, overlap is maintained while a conformation with the $C^{3\beta}$H in a favourable orientation for migration is now possible (Fig.15.).

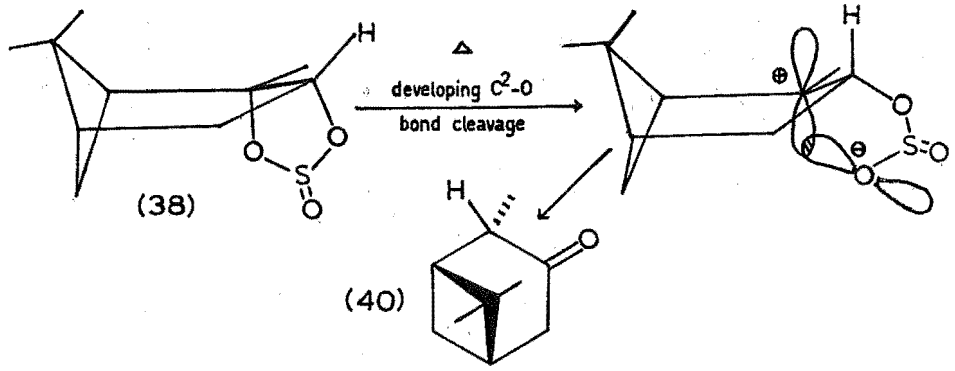


Fig.15.

In an attempt to further define the factors which affect the course of these rearrangements in terpenoid systems the 2-phenylbornane system was examined. In this the initially formed carbonium ion will be classical (no σ-bond delocalization as distinct from π-delocalization) and greater steric constraints may be expected. In addition the rearrangement of cis- and trans-butene epoxides (108 and 109) and the butan-2,3-diol cyclic sulphites (116 and 117) were examined. The results from these model systems should aid in the interpretation of the cyclic sulphite and epoxide rearrangements in general.

DISCUSSION

Preparation and Stereochemistry of the Phenyl Grignard Alcohol (46) from Camphor

The determination of the stereochemistry at C^2 for the phenyl Grignard alcohol (46) derived from D-(+)-camphor (43) is important, since this should facilitate the determination of the stereochemistry of the 2,3-epoxy-2-phenylbornanes (49 and 50) *via* LAH reduction to the alcohols (46 and 48). Alternatively, if the epoxide configuration at C^2 is known and hence the alcohols (46 and 48) formed by LAH reduction; then the identity of the phenyl Grignard alcohol (46) to one of them, would demonstrate the stereochemistry of phenylmagnesium bromide attack at camphor. The known stereochemistry of this alcohol would also facilitate the interpretation of NMR spectra of phenyl substituted bicyclo[2.2.1]heptanes.

Reaction of camphor with phenylmagnesium bromide[29], *p*-anisylmagnesium bromide[30] or phenyllithium[31] gives rise to a *tert.*-alcohol in *ca.* 23% yield. This low yield is attributed to the irreversible formation of the enol salt[32,33]. In the preparation of the phenyl alcohol (46; 20%) Bernstein[32] reported the formation of 1-phenylcamphene (66; 11%) from the phenylmagnesium-camphor complex (51).

In our hands less than 1% of 1-phenylcamphene (66) was formed. An attempt to isolate the epimeric alcohol (48) by chromatography and NMR studies gave no evidence for its

formation.

The reaction of camphor with a series of Grignard reagents is reported[33] to be virtually stereospecific, with the formation of only traces of the epimeric alcohol in each case. The assignment of the alkyl group as endo- is inferred from the following observations. Δ^5-Camphor (52) on reaction with methylmagnesium iodide gives a Δ^5-alcohol (53)[113]. The stereochemistry is suggested to be endo- from steric considerations. The identity of the hydrogenated Δ^5-alcohol (53) with the alcohol derived from camphor suggests the alkyl group to be endo-.

In order to prove unequivocally the endo-attack of a phenyl group several methods were investigated:

(1). For the phenyl alcohol (46) with an exo-hydroxyl it should be possible to effect the formation of the ether (54) by reaction with $Pb(OAc)_4$ in methylcyclohexane[34] or by reaction with $HgO-Ag_2O-Br_2$ in n-pentane[35]. However no trace of the ether (54) could be isolated from these reactions.

(2). Reduction of the 2-exo-hydroxy-2-endo-phenylbornan-3-one thioketal (56) with Raney Ni should give the 2-exo-hydroxy-2-endo-phenylbornane (46). This approach however could not be used because of difficulties encountered in the formation of the thioketal (56) from the unreactive ketol.

(3). LAH reduction of the 2-hydroxy-3-tosylates (60) and (62) might be expected to give (46) and (48) respectively (cf.[36,37]). The 2-endo-hydroxy-3-exo-tosylate (62; 88%) was

prepared by treatment of the trans-diol (61) with p-tolylsulphonyl chloride. This product was identified by its IR spectum which exhibited absorptions at 3598 cm^{-1} (OH), 1370, 1190 and 1178 cm^{-1} (-O-SO_2-) and the NMR spectrum which showed the C^{3}-endo-H as a singlet at δ 4.63 ppm ($J_{3\text{-endo-H},4\text{-H}}$ ~ 0 Hz), the tolyl-Me as a singlet at δ 2.27 ppm and the $C^{10}H_3$, $C^{8}H_3$ and $C^{9}H_3$ at δ 1.16, 1.08 and 0.98 ppm. The 2-exo-hydroxy-3-exo-tosylate (60; 95%) was similarly prepared from the cis-diol (59). The product was identified by its IR spectrum which showed absorptions at 3586, 3518 cm^{-1} (OH), 1373, 1189 and 1176 cm^{-1} (-O-SO_2-) and the NMR spectrum which showed the C^{3}-endo-H as a singlet at δ 5.04 ppm ($J_{3\text{-endo-H},4\text{-H}}$ ~ 0 Hz), the tolyl-Me as a singlet at δ 2.39 ppm along with the $C^{8}H_3$ at δ 1.34 ppm and the $C^{9}H_3$ and $C^{10}H_3$ at δ 0.87 ppm.

Reduction of 2-endo-hydroxy-3-exo-tosylate (62) gave 3-endo-hydroxy-2-endo-phenylbornane (99; 30%) identical with an authentic sample.

Reduction of the 2-exo-hydroxy-3-exo-tosylate (60) gave mainly a tert.-alcohol (65; 43%). The physical data (elemental analysis, IR and UV) was consistent with the tert.-alcohol (46).

$SOCl_2$-Pyridine dehydration of the alcohol (65) gave a complex mixture containing no 1-phenylcamphene (66) or 2-phenylbornylene (72) hence the alcohol structure (46) seems doubtful. LAH reduction of a series of substituted bicyclo[2.2.2]octane tosylates (63) has been reported[38] to give the compounds (64) (Fig. 16.). The tert.-alcohol could have the

structure (65) as a result of a similar 1,2-skeletal migration (Fig.16b.). The NMR spectrum of 65 which exhibited the C^2Me as a sharp singlet at δ 1.07 provides additional evidence for this structure since the syn-hydroxyl deshields the $C^{3\text{-exo-}}$Me (δ 1.22 ppm) by 0.22 ppm in relation to the $C^{3\text{-endo-}}$Me (δ 1.00 ppm). 7-syn-Hydoxy-1-phenylcamphene (68) exhibits a similar shift (0.21 ppm).

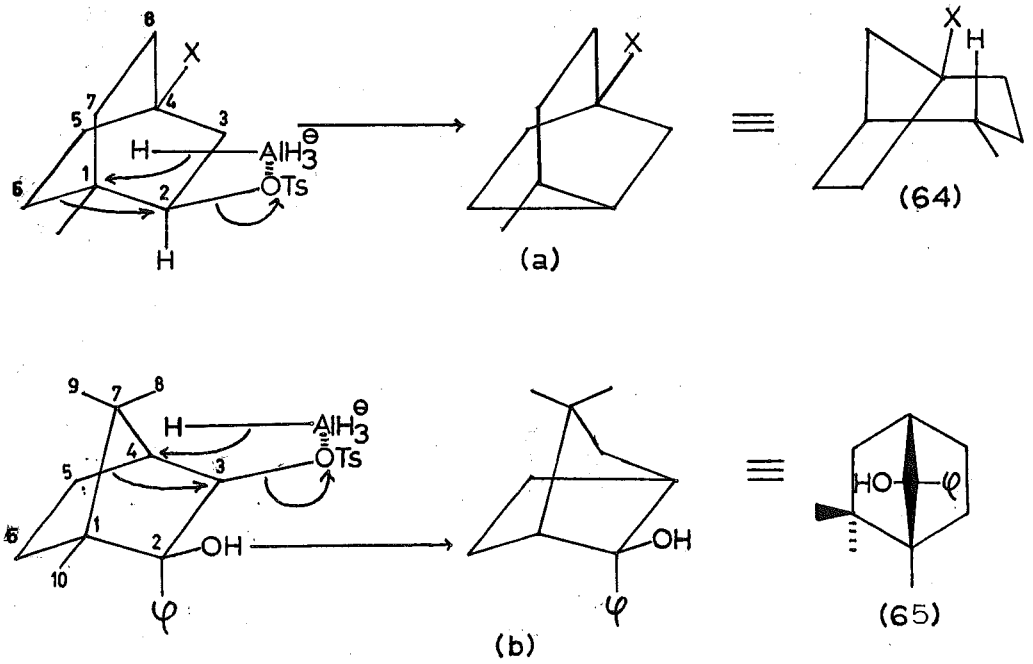


Fig.16.

(4). Oxymercuration followed by in situ $NaBH_4$ demercuration provides a convenient method for Markownikov hydration of an olefin[39-41]. In the oxymercuration-demercuration of norbornylene (73)[41], apobornylene (76)[41], 1-methylnorbornylene (74)[41], 4-methylbornylene (78)[42] and 2-phenylnorbornylene (75)[43] the products found are those derived by nucleophilic attack at the exo-face of the postulated mercurinium ion (79)[44]. Hence

reaction of 2-phenylbornylene (72) in the presence of H_2O as a nucleophile may be expected to give 2-exo-hydroxy-2-endo-phenylbornane (46).

The oxymercuration-demercuration reaction of 2-phenylbornylene (72) in THF gave however the divinyl mercury (80; 61%) in addition to starting material (72; 21%)[45]. The assignment of the divinyl mercury structure (80) to the major product was based on the following evidence. The presence of mercury in the compound was confirmed by the isotopic structure of the parent ion peaks in the mass spectra. Elemental analysis and accurate mass measurement of the parent ion of the divinyl mercury (80) were consistent with a molecular formula $C_{32}H_{38}Hg$. The simplicity of the NMR spectrum with the C^4H as a doublet centred at δ 2.38 ppm ($J_{4\text{-}H,5\text{-}exo\text{-}H}$ 3.0 Hz) and the $C^{10}H_3$, C^9H_3 and C^8H_3 as singlets at δ 0.99, 0.84 and 0.78 ppm respectively implied an element of symmetry. The UV exhibited absorptions at 225 nm (ϵ 4160), 246 nm (ϵ 4140) and 280 nm (ϵ 4140) and the absence of olefinic protons in the NMR spectrum showed the presence of a tetrasubstituted double bond probably conjugated with the phenyl group. Confirmation of this structure was based on LAH reduction of the divinyl mercury (80) to give 2-phenylbornylene (72; 94%).

In order to establish at which point the reaction was anomalous the reaction was repeated in two discrete steps. Oxymercuration of 2-phenylbornylene (72) in THF gave the vinyl mercury acetate (81; 88%). This product was identified on the

following evidence. The presence of mercury in the compound was confirmed by the isotopic structure of the parent ion peaks in the mass spectra. Elemental analysis and accurate mass measurement of the parent ion of the vinyl mercury acetate (81) were consistent with the molecular formula $C_{17}H_{22}HgO_2$. The NMR spectrum exhibited the C^4H as a doublet centred at δ 2.49 ppm ($J_{4-H,5-\underline{exo}-H}$ 3.0 Hz), the C^3HgOAc as a singlet at δ 1.98 ppm along with the $C^{10}H_3$, C^8H_3 and C^9H_3 as singlets at δ 1.02, 0.94 and 0.83 ppm respectively. The tetrasubstituted double bond conjugated with the phenyl group is consistent with the absence of olefinic protons in the NMR spectrum and the UV spectrum which exhibited absorptions at 227 nm (ϵ 10700) and 265 nm (ϵ 7710).

Attempted demercuration in THF or MeOH with $NaBH_4$ gave the divinyl mercury (80) in 69% and 90% yields respectively[45].

The oxymercuration reaction is thought to involve equilibrium formation of the mercurinium ion (79) followed by rate determining rearrangement or nucleophilic attack involving a transition state where considerable positive charge is localized at the C^1 carbon atom[44] (Fig.17.).

The absence of rearranged products in the oxymercuration of 2-phenylbornylene (72) is probably a reflection of some Hg stabilization of the C^2 carbonium ion.

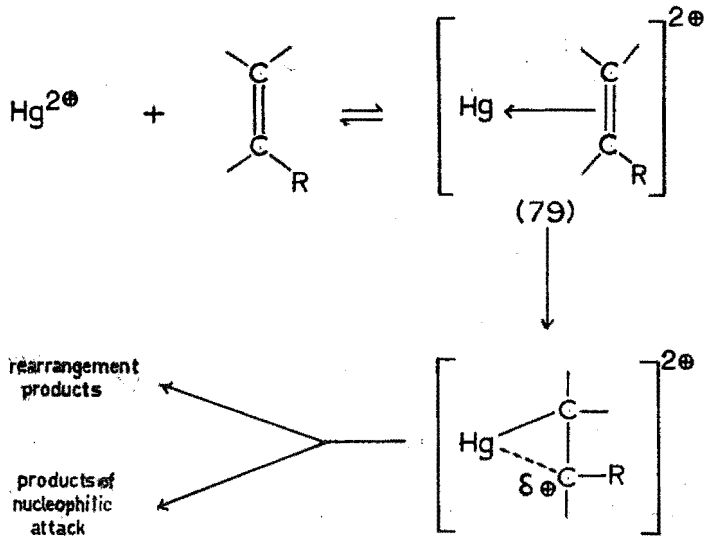


Fig.17.

The mechanism of formation of the vinyl mercury acetate (81) is thought to involve formation of the exo-mercurinium ion with subsequent proton loss (Fig.18.).

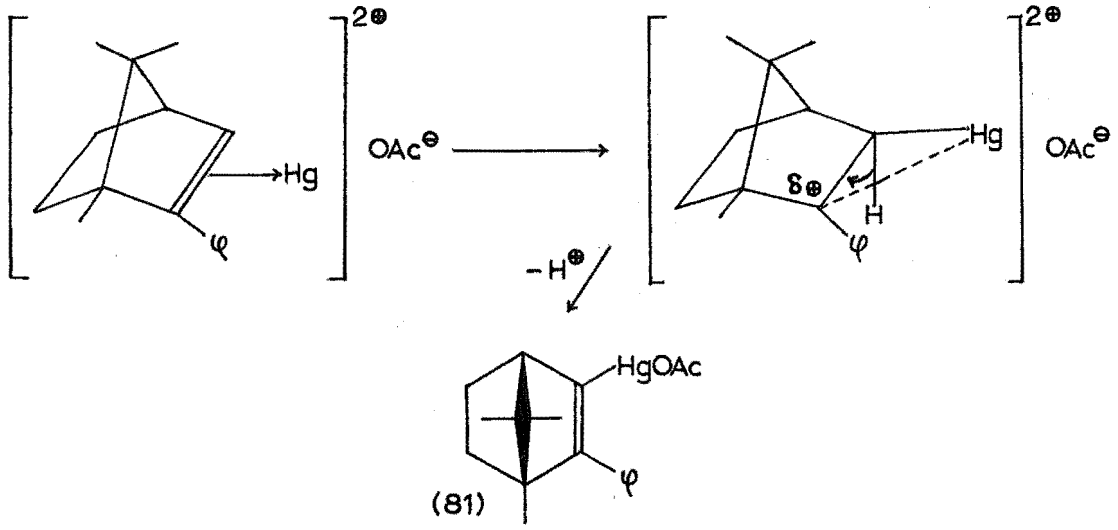


Fig.18.

This type of proton loss to give a vinyl mercury acetate is considered to occur in those systems where a tertiary carbonium ion may be formed, and where because of its hindered environment it would be shielded from nucleophilic attack by a water molecule (see Appendix A).

The $NaBH_4$ reduction of alkyl mercury acetates normally gives rise to demercuration[39-43]. This process is thought to involve formation of the alkyl mercury hydride followed by decomposition by a free radical mechanism and subsequent product formation[46] (Fig.19.).

$$RHgOAc \xrightarrow{NaBH_4} RHgH \longrightarrow R^{\bullet} + {}^{\bullet}HgH \longrightarrow RH + Hg$$

Fig.19.

Partial demercuration of the vinyl mercury acetate by $NaBH_4$ reduction to the divinyl mercury (80) lends support to the intervention of radical intermediates (Fig.20.).

The divinyl mercury (80) once formed seems to be relatively inert towards further reduction by $NaBH_4$ in the aqueous medium. An attempt to observe the ESR spectrum of the proposed 2-phenyl-bornylene radical intermediate was unsuccessful.

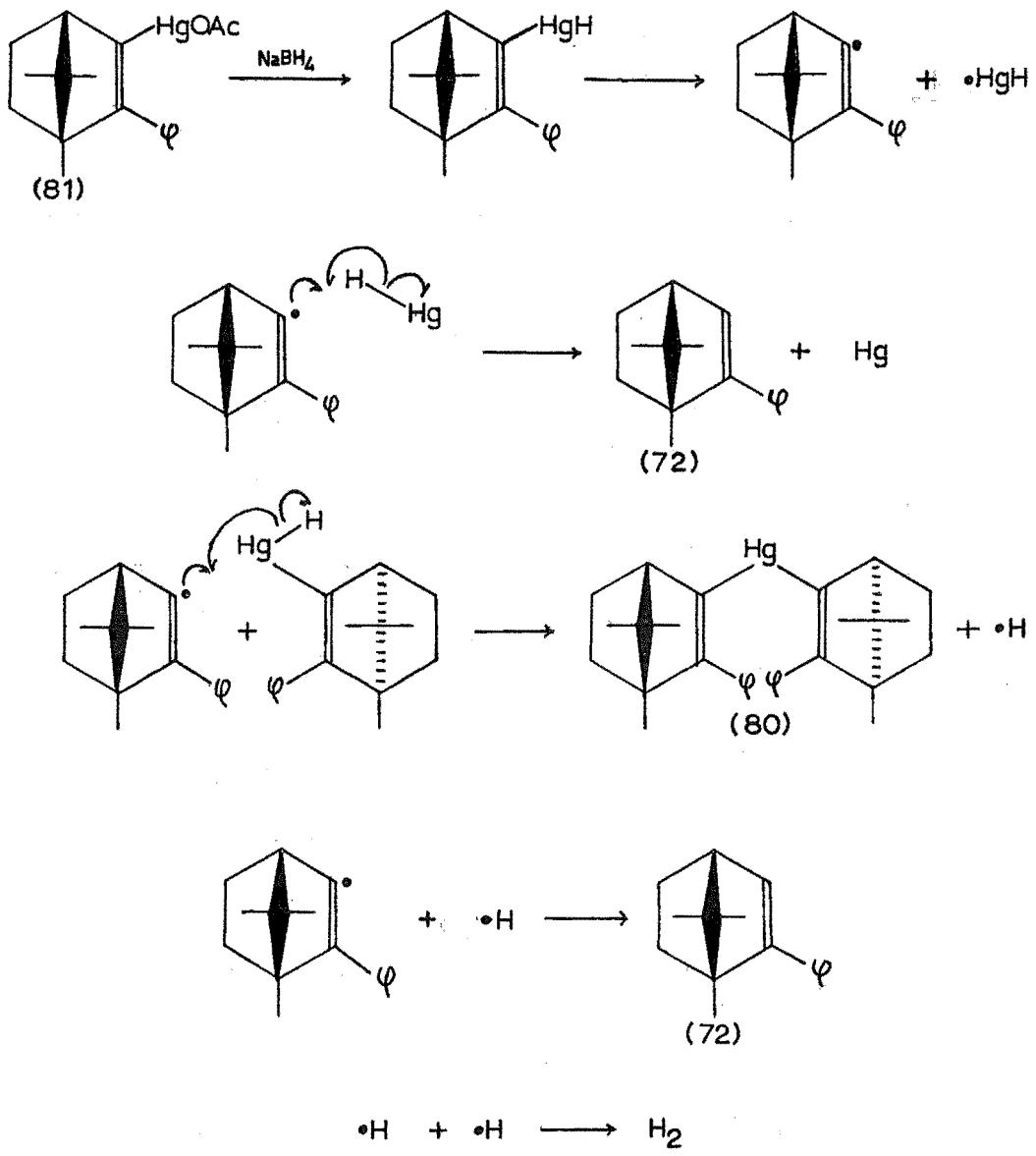


Fig.20.

(5). LAH reduction of the 2,3-epoxy-2-phenylbornanes (49 or 50) should give the alcohols (46 or 48) (cf. ref. 47.). However prolonged treatment of the exo-epoxide (49) gave only unreacted epoxide (49) (cf. ref. 48. and 70.). Li-$EtNH_2$ reduction of the exo-epoxide (49) (cf. ref. 48 and 70.) gave

2-endo-cyclohexyl-3-exo-hydroxybornane (97) identified by its IR spectrum which showed an absorption at 3605 cm^{-1} (OH) and its NMR spectrum which exhibited the olefinic proton at δ 5.45 ppm ($W_{h/2}$ 6 Hz), the $C^{3\text{-exo-}}H$ as a doublet centred at δ 3.81 ppm ($J_{2\text{-exo-}H,3\text{-endo-}H}$ 4.6 and $J_{3\text{-endo-}H,4\text{-}H}$ ~ 0 Hz), the $C^{2\text{-exo-}}H$ as a broad doublet centred at δ 2.35 ppm ($J_{2\text{-exo-}H,3\text{-endo-}H}$ 4.6 and $J_{2\text{-exo-}H,6\text{-exo-}H}$ > 0 Hz) along with the $C^{8}H_3$ at δ 1.14 ppm and the $C^{9}H_3$ and $C^{10}H_3$ at δ 0.83 ppm. Confirmation of this structure (96) was obtained by Li-$EtNH_2$ reduction of 3-exo-hydroxy-2-endo-phenylbornane (96) which gave the same product (97). This series of reductions provides evidence of the exo-configuration of the epoxide ring in 49.

(6). Direct evidence of the exo-hydroxyl configuration for the phenyl Grignard alcohol (46) has been obtained from the $SOCl_2$-pyridine dehydration of 3-exo-deutero-2-hydroxy-2-phenylbornane (47) to give 2-phenylbornylene (72)[49]. 3-exo-Deuterocamphor (44; 31% d_1) was prepared from D-(+)-camphor (43)[14,50]. Reaction of this ketone (44) with phenylmagnesium bromide gave 3-exo-deutero-2-hydroxy-2-phenylbornane (47; 48% d_1; 34%). The deuterium content in the 3-exo-position was enhanced relative to 3-exo-deuterocamphor (44; 31% d_1) presumably as a result of the deuterium isotope effect on the formation of the enol salt[33]. Dehydration of the 3-exo-deutero-2-hydroxy-2-phenylbornane (47; 48% d_1) gave in high yield (89%) a mixture of 2-phenylbornylene (72) and 7-syn-deutero-1-phenylcamphene (67) in the ratio 86:14 containing 10% d_1. After compensating

for the deuterium content in the 7-syn-deutero-1-phenylcamphene (67) the resulting d_1 content in 2-phenylbornylene (72) was ca. 4.0%. 2-Phenylbornylene (72) isolated by chromatography on silica gel showed a d_1 content of ca. 3.5%. Assuming dehydration of the alcohol (47) by $SOCl_2$-pyridine involves formation of the chlorosulphite ester followed by bimolecular syn-elimination[51,52] the loss of the 3-exo-deuterium implies that the hydroxyl group has the exo-configuration. The 7-syn-deutero-1-phenylcamphene (67) presumably arises by collapse of the chlorosulphite ester and a Wagner-Meerwein rearrangement, followed by loss of a proton. Acid catalysed dehydration (chromatography on silica gel) of the alcohol (46) gives predominantly 1-phenylcamphene (66; 85%).

Preparation of 2-Phenylbornylene (72)

2-Phenylbornylene (72) has been prepared via the Chugaev reaction on 2-exo-hydroxy-2-endo-phenylbornane (46)[31]. In general the Chugaev reaction involves the formation of the sodium[53], potassium[53] or lithium[31] alkoxide followed by addition of CS_2 to give the sodium xanthate. Reaction of the sodium xanthate with an alkyl halide then gives the alkyl xanthate which on pyrolysis affords the olefin resulting from cis-β-hydrogen elimination[54-57] (Fig.21.).

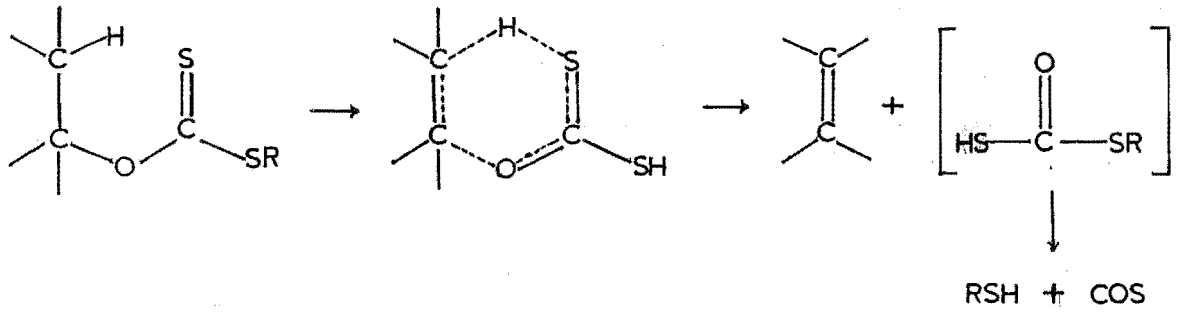


Fig.21.

For the preparation of 2-phenylbornylene (72) the S-ethyl xanthate (84) was prepared via the sodium xanthate (83) prepared from the action of CS_2 on the sodium alkoxide (82). Pyrolysis of the crude S-ethyl xanthate (84) afforded a crude mixture containing 2-phenylbornylene (72) and 1-phenylcamphene (66) in the ratio 19:1. Chromatography on silica gel gave 2-phenylbornylene (72) > 98% pure. Spinning band distillation of this material gave the olefin (72) > 99% pure. Due to the difficulty in forming the sodium alkoxide (82) the overall yield of olefin (72) was low (47%).

A considerably simpler and more elegant preparation of 2-phenylbornylene (72) involves the $SOCl_2$-pyridine dehydration of the alcohol (46) giving a (17:3) mixture of 2-phenylbornylene (72) and 1-phenylcamphene (66). Purification of the olefin (72) was effected by chromatography and spinning band distillation as above.

Attempted Preparation of 2,3-Epoxy-2-phenylbornanes (49 and 50)

(1). Peracid oxidation of 2-phenylbornylene (72)

Reaction of olefins with peracids provides a convenient

method of preparing epoxides. Two mechanisms for this peracid oxidation reaction have been suggested. Bartlett[58] postulated a "molecular" mechanism (Fig.22a.) while Kwart and Hoffman have proposed a 1,3-dipolar addition (Fig.22b.).

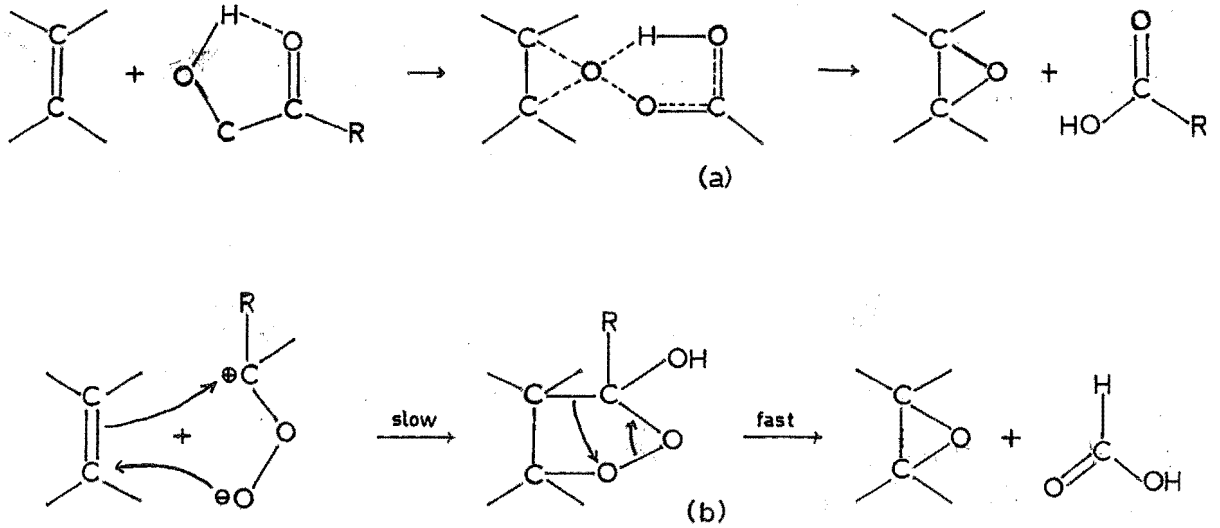


Fig.22.

No experimental evidence presently available can be used to determine which of these mechanisms is operating.

Reaction of 2-phenylbornylene (72) with m-chloroperbenzoic acid in $CHCl_3$ gave a complex mixture separated by chromatography on activated alumina. In addition to starting material (72; 0.3%), the products in order of elution were 1-phenylcamphene epoxide (85; 1%), 2-endo-phenylbornan-3-one (87; 41%), 7-syn-hydroxy-1-phenylcamphene epoxide (86; 2%), 3-exo-hydroxy-2-phenyltricyclene (89; 14%) and an unknown (12%).

1-Phenylcamphene epoxide (85) was identified by its NMR spectrum. This spectrum exhibited the epoxide methylene protons as an AB quartet δ 2.49 and 1.95 ppm (J_{AB} 4.8 Hz).

The $C^{3\text{-}\underline{exo}}$-Me was deshielded by the neighbouring oxygen to δ 1.04 ppm while the $C^{3\text{-}\underline{endo}}$-Me was at δ 0.90 ppm. This compound is thought to arise from peracid oxidation of 1-phenylcamphene (66) present as an impurity (< 1%) in the 2-phenylbornylene (72) used. The stereochemistry of the epoxide ring as _exo_- is assigned on the known preference of _exo_-face attack on camphene (130)[116].

The major product 2-_endo_-phenylbornan-3-one (87) was identified by its IR spectrum which showed an absorption at 1746 cm^{-1} (C=O) and its NMR spectrum which exhibited the $C^{2\text{-}\underline{exo}}$-H as a singlet at δ 3.49 ppm ($W_{h/2}$ 3 Hz; $J_{2\text{-}\underline{exo}\text{-H},\ 6\text{-}\underline{exo}\text{-H}} > 0$ Hz), the C^4H as a doublet centred at δ 2.36 ppm ($J_{4\text{-H},5\text{-}\underline{exo}\text{-H}}$ 4.4 Hz) along with the three methyls (C^8H_3, C^9H_3 and $C^{10}H_3$) as singlets at δ 1.09, 1.05 and 0.99 ppm. The ORD spectrum showed a molecular amplitude _a_ = -24.5. The C^2-epimeric ketone (88) under identical reaction conditions to peracid oxidation did not epimerise to 87 and therefore the ketone (87) must be considered as a primary product of the reaction.

7-_syn_-Hydroxy-1-phenylcamphene epoxide (86) was identified from the NMR spectrum which exhibited the $C^{7\text{-}\underline{anti}}$-H as a doublet centred at δ 4.51 ppm ($J_{4\text{-H},7\text{-}\underline{anti}\text{-H}}$ 1.6 Hz[61]), the epoxide methylene as an AB quartet δ 2.70 and 2.27 ppm (J_{AB} 4.6 Hz). The singlets due to the $C^{3\text{-}\underline{exo}}$-Me and the $C^{3\text{-}\underline{endo}}$-Me were located at δ 1.27 and 1.01 ppm respectively. The position of the methyl signals indicates that the 7-hydroxyl group has a

syn-relationship with respect to the methyls as a result of the hydroxyl deshielding the $C^{3-\underline{exo}-}Me$.

The IR spectrum 3604 cm^{-1} (OH), UV spectrum and elemental analysis were consistent with this structure (86). The mode of formation of the epoxy-alcohol (86) is considered to involve initial peracid attack, rearrangement of the intermediate to the hydroxy-olefin (68) followed by peracid attack from the exo-face. Exo-face attack should be favoured as a result of the decreased torsional barrier (cf. endo-attack) and as a result of hydrogen bonding to the $C^{7-\underline{syn}-}OH$ (Fig.23.).

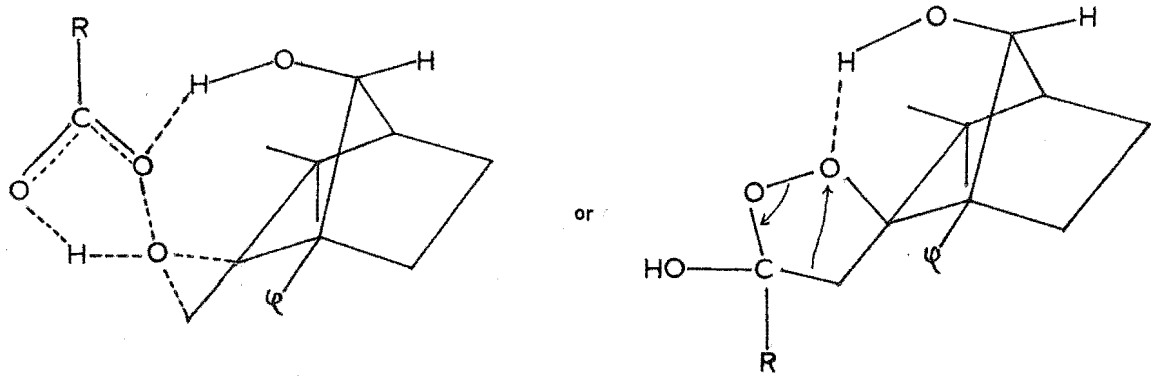


Fig.23.

3-exo-Hydroxy-2-phenyltricyclene (89) was identified by the NMR spectrum which showed the $C^{3-\underline{endo}-}H$ as a doublet centred at δ 4.48 ppm ($J_{3-\underline{endo}-H,4-H}$ 1.8 Hz). The three methyls $C^{8}H_3$, $C^{9}H_3$ and $C^{10}H_3$ exhibited singlets at δ 1.03, 0.92 and 0.83 ppm respectively. The IR spectrum demonstrates the prescence of the hydroxyl by an absorption at 3614 cm^{-1}. The UV spectrum and accurate mass measurement of the parent ion

peak were consistent with the structure (89). The mode of formation of this product (89) is uncertain.

The final product was a compound with an accurate mass measurement of the parent ion peak consistent with a molecular formula $C_{15}H_{20}O_2$. The IR spectrum showed absorptions at 3638 cm^{-1} (OH), 759 and 699 cm^{-1} (monosubstituted benzene) but no carbonyl. The UV and NMR spectra were consistent with the presence of a monosubstituted benzene. The NMR spectrum exhibited a quartet centred at δ 3.71 ppm (J 7.6 and J' 6.2 Hz; 1H), a singlet at δ 1.66 ppm (OH) and three methyls as singlets at δ 1.20, 1.07 and 0.90 ppm. The signal at δ 3.71 ppm is considered to arise from a proton geminal to an ether linkage. The identity of this compound remains unknown.

The peracid oxidation was also carried out in CCl_4 (Table.3.).

Table.3.

m-Chloroperbenzoic acid Oxidation of 2-Phenylborn-2-ene (72)

Product	% Yield Solvent		Result of endo-(N) or exo-(X) attack
	$CHCl_3$	CCl_4	
2-Phenylbornylene (72)	0.3	-	-
1-Phenylcamphene epoxide (85)	1	1	-
2-endo-Phenylbornan-3-one (87)	41	47	-
7-syn-Hydroxy-1-phenylcamphene epoxide (86)	2	2	N
3-exo-Hydroxy-2-phenyltricyclene (89)	14	6	X
Unknown	12	10	X

Table.4.

Percentages of *endo*- and *exo*-Attack

Solvent			
$CHCl_3$		CCl_4	
exo-	*endo*-	*exo*-	*endo*-
32±9	68±9	20±8	80±8

Epoxidation of norbornene (73) gave 99.5% of the *exo*-epoxide (101) in contrast to apobornylene (76) which gave only 10% of the *exo*-epoxide (102)[62]. The stereochemistry of attack is largely governed by the steric hindrance of the 7,7-*gem*-dimethyls. The greater proportion of *exo*-attack for 2-phenylbornylene (72) (Table.4.) relative to apobornylene reflects the greater torsional effect, between the C^1-Me and C^2-phenyl bonds relative to the C^1-H and C^2-H bonds in apobornylene (76).

(2). NBS - aq. DMSO on 2-Phenylbornylene (72)

An attempt was made to prepare the 2-phenylbornylene bromohydrin (90) which on base catalysed elimination might give 2,3-epoxy-2-phenylbornane.

A convenient preparation of bromohydrins from olefins is described by Dalton et al[63] using NBS - aq. DMSO. However reaction of 2-phenylbornylene (72) with NBS - aq. DMSO gave no detectable trace of the bromohydrin (90).

The main product (78% by GLC) isolated by crystallization was identified as 7-*anti*-bromo-1-phenylcamphene (70). The

structural assignment was based on the NMR spectrum which exhibited the C^{7}-<u>syn</u>-H as a broad singlet at δ 4.72 ppm ($W_{h/2}$ 4 Hz; $J_{4\text{-}H,7\text{-}\underline{syn}\text{-}H} > 0$ Hz), the C^{2} exocyclic methylene as singlets at δ 4.70 and 4.22 ppm and the C^{3}-<u>endo</u>-Me and C^{3}-<u>endo</u>-Me as singlets at δ 1.24 and 1.20 ppm respectively. The IR spectrum showed an absorption at 893 cm^{-1} (exocyclic methylene) while the elemental analysis was consistent with a molecular formula $C_{16}H_{19}Br$. The deshielding by 0.04 ppm of the C^{3}-<u>exo</u>-Me by the C^{7}-<u>anti</u>-Br relative to the C^{3}-<u>endo</u>-Me in contrast to the deshielding of 0.21 ppm for 7-<u>syn</u>-hydroxy-1-phenylcamphene (68) establishes the bromine stereochemistry at C^{7} (cf. 6βBr on the $C^{19}H_{3}$ of 0.25 ppm in steroids[64]).

The product arises from <u>endo</u>-attack to form the bromonium ion followed by Wagner-Meerwein rearrangement in preference to nucleophilic attack by a hydroxyl ion (Fig.24.) (cf. oxymercuration of 2-phenylbornylene p. 20).

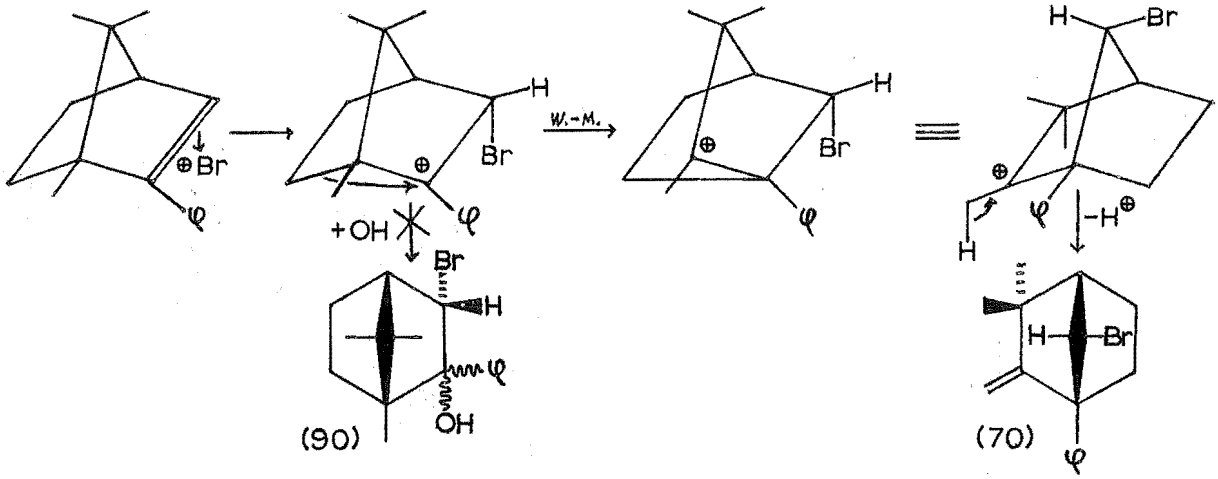


Fig.24.

The predominance of <u>endo</u>-attack is indicative of the

steric influence imposed by the C^7-gem-dimethyls.

Further reaction of 7-anti-bromo-1-phenylcamphene (70) with NBS - aq. DMSO gave 3,10-dibromo-2-phenylbornylene (91; 95%) which was a minor product (8% by GLC) in the NBS - aq. DMSO reaction on 2-phenylbornylene (72). The structure follows from the NMR spectrum which exhibited the $C^{10}H_2Br$ as a singlet at δ 3.58 ppm, the C^4H as a doublet centred at δ 2.56 ($J_{4-H,5\text{-exo-}H}$ 2.7 Hz) along with the C^8H_3 and C^9H_3 as singlets at δ 1.18 and 1.03 ppm. The absence of olefinic protons in the NMR spectrum and the UV spectrum which showed an absorption at λ_{max} 247 nm (ϵ 6500) indicated a tetrasubstituted double bond conjugated to the phenyl group. The elemental analysis was consistent with a molecular formula $C_{16}H_{18}Br_2$.

The product is envisaged as arising from 7-anti-bromo-1-phenylcamphene (70) via a Wagner-Meerwein rearrangement followed by proton loss (Fig.25.).

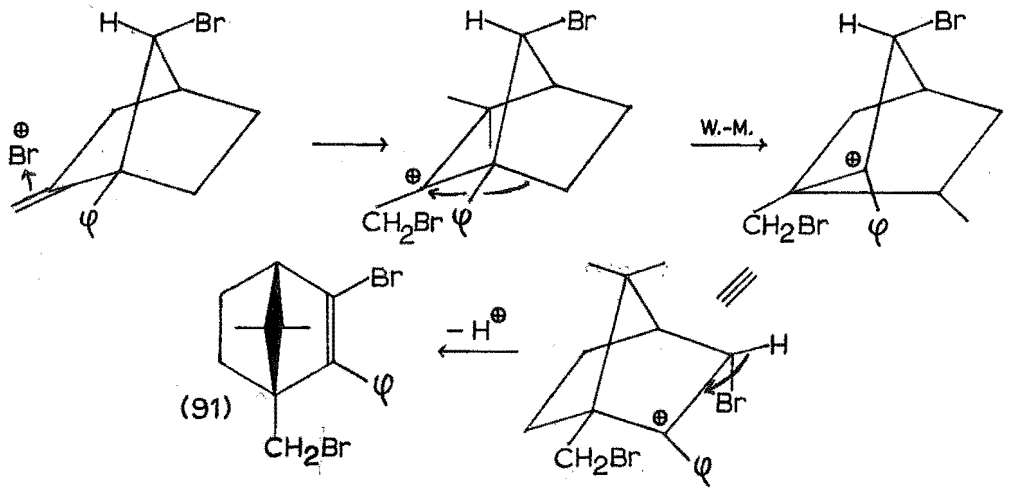


Fig.25.

Hydroboration of 2-Phenylbornylene (72)

In order to determine whether the 2-endo-phenylbornan-3-one (87) was a primary product of the rearrangements of the epoxides (49 and 50) and the cyclic sulphites (95a and 95b) and in the reaction of m-chloroperbenzoic acid on 2-phenylbornylene (72) it was necessary to synthesize the 2-exo-phenylbornan-3-one (88). This was achieved by hydroboration followed by alkaline hydrogen peroxide oxidation to give some 3-endo-hydroxy-2-exo-phenylbornane (98) which could be oxidised to 88.

The formation of 3-exo-hydroxy-2-endo-phenylbornane (96) was of value in providing chemical proof of the exo-epoxide (49) stereochemistry since reaction of the exo-epoxide with Li-$EtNH_2$ had been shown to give an alcohol (97). The correctness of the assignment of structure 97 to the alcohol was confirmed by Li-$EtNH_2$ reduction of 96 to give 2-endo-cyclohexyl-3-exo-hydroxybornane (97).

The hydroboration and alkaline hydrogen peroxide oxidation of 2-phenylbornylene (72), in contrast to the oxymercuration of 72 and the reaction of NBS - aq. DMSO with the olefin (72), gave the normally expected products (96 and 98).

Hydroboration of olefins is known to occur via a cis-1,2-addition to give di- and tri-alkylated boranes [65] (Fig.26.).

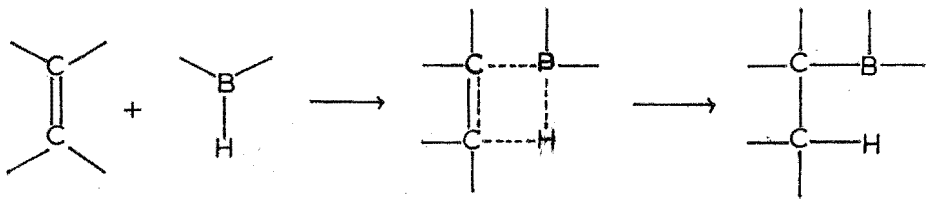


Fig.26.

Oxidation *in situ* by alkaline hydrogen peroxide affords the alcohol where the hydroxyl group has the same stereochemistry as the boron atom in the alkylborane (Fig.27.).

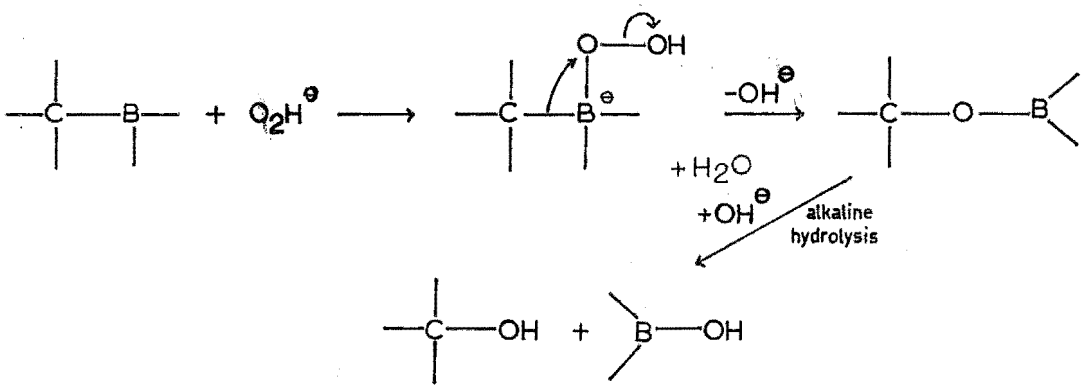


Fig.27.

Formation of the alkylboranes followed by heating has been found to effect equilibration of alkylboranes to give the thermodynamically more stable product.

Hydroboration of 2-phenylbornylene (72) followed by *in situ* alkaline hydrogen peroxide oxidation gave in addition to starting material (72; 1%) and 2-*exo*-hydroxy-2-*endo*-phenylbornane (46; 3%) two major products 3-*exo*-hydroxy-2-*endo*-phenylbornane (96; 38%) and 3-*endo*-hydroxy-2-*exo*-phenylbornane (98; 48%) separable by chromatography on activated alumina.

The least polar major product was identified as 3-*exo*-hydroxy-2-*endo*-phenylbornane (96) from the IR spectrum which showed an absorption at 3589 cm^{-1} (OH) and NMR spectrum which exhibited the C^{3}-*endo*-H as a doublet centred at δ 4.15 ppm

($J_{2\text{-}\underline{exo}\text{-}H,3\text{-}\underline{endo}\text{-}H}$ 4.4 Hz) and the $C^{2\text{-}\underline{exo}}\text{-}H$ as a quartet centred at δ 3.09 ppm ($J_{2\text{-}\underline{exo}\text{-}H,3\text{-}\underline{endo}\text{-}H}$ 4.4 and $J_{2\text{-}\underline{exo}\text{-}H,6\text{-}\underline{exo}\text{-}H}$ 1.7 Hz). The C^8H_3, C^9H_3 and $C^{10}H_3$ exhibited singlets at δ 1.27, 0.93 and 0.75 ppm respectively.

CrO_3-Pyridine oxidation of this alcohol (96) gave 2-endo-phenylbornan-3-one (87; 88%) identical with an authentic sample.

LAH reduction of this endo-phenyl ketone (87) gave 3-endo-hydroxy-2-endo-phenylbornane (99; 78%). This product was identified by its IR spectrum which showed an absorption at 3609 cm^{-1} (OH) and the NMR spectrum which exhibited the $C^{3\text{-}\underline{endo}}\text{-}H$ as an octet centred at δ 4.56 ppm ($J_{2\text{-}\underline{exo}\text{-}H,3\text{-}\underline{exo}\text{-}H}$ 9.9, $J_{3\text{-}\underline{exo}\text{-}H,4\text{-}H}$ 4.1 and $J_{3\text{-}\underline{exo}\text{-}H,5\text{-}\underline{exo}\text{-}H}$ 1.2 Hz), the $C^{2\text{-}\underline{exo}}\text{-}H$ as a quartet centred at δ 3.07 ppm ($J_{2\text{-}\underline{exo}\text{-}H,3\text{-}\underline{exo}\text{-}H}$ 9.9 and $J_{2\text{-}\underline{exo}\text{-}H,6\text{-}\underline{exo}\text{-}H}$ 1.9 Hz). The C^8H_3, C^9H_3 and $C^{10}H_3$ exhibited singlets at δ 1.05, 0.99 and 0.65 ppm respectively.

The major product (48%) of hydration was identified as 3-endo-hydroxy-2-exo-phenylbornane (98) by its IR spectrum which showed an absorption at 3592 cm^{-1} (OH) and NMR spectrum which exhibited the $C^{3\text{-}\underline{exo}}\text{-}H$ as an octet centred at δ 4.92 ppm ($J_{2\text{-}\underline{endo}\text{-}H,3\text{-}\underline{exo}\text{-}H}$ 6.5, $J_{3\text{-}\underline{exo}\text{-}H,4\text{-}H}$ 3.7 and $J_{3\text{-}\underline{exo}\text{-}H,5\text{-}\underline{exo}\text{-}H}$ 1.1 Hz) and the $C^{2\text{-}\underline{endo}}\text{-}H$ as a doublet centred at δ 2.57 ppm ($J_{2\text{-}\underline{endo}\text{-}H,3\text{-}\underline{exo}\text{-}H}$ 6.5 Hz). The $C^{10}H_3$, C^9H_3 and C^8H_3 exhibited singlets at δ 0.99, 0.88 and 0.70 ppm respectively.

CrO_3-Pyridine oxidation of this alcohol (98) gave 2-exo-phenylbornan-3-one (88; 85%) identified on the following

evidence. The IR spectrum exhibited an absorption at 1743 cm^{-1} (C=O). The UV spectrum showed an absorption at 280-296 nm (ϵ 41) to 328 nm (ϵ 9). The NMR spectrum exhibited the C^{2}-endo-H as a singlet at δ 3.37 ppm along with the three methyls ($C^{8}H_3$, $C^{9}H_3$ and $C^{10}H_3$) as singlets at δ 0.99, 0.96 and 0.95 ppm. The ORD spectrum showed a molecular amplitude a = -24.2. The stereochemical assignment is based on the stereochemistry of the alcohol (98) and the epimerisation of this ketone (88) to its C^{2} epimer (87) on treatment with base, or chromatography on activated or 10% deactivated alumina.

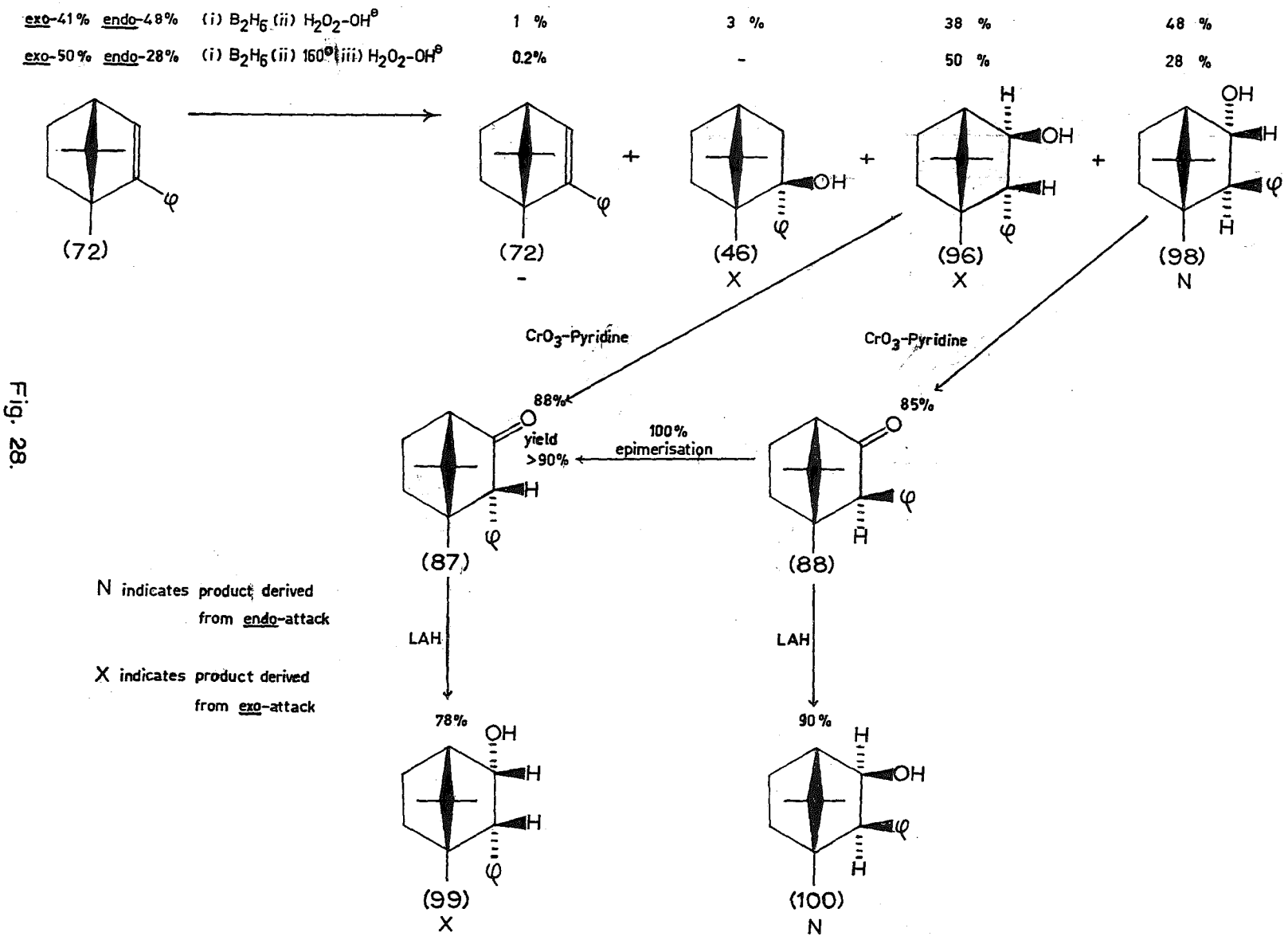
LAH reduction of this exo-phenyl ketone (88) to 3-exo-hydroxy-2-exo-phenylbornane (100; 90%) confirmed this structure. The identity of this 3-exo-hydroxy-2-exo-phenylbornane follows from the IR spectrum which showed an absorption at 3579 cm^{-1} (OH) and NMR spectrum which exhibited the C^{3}-endo-H as a doublet centred at δ 4.12 ppm ($J_{2\text{-endo-H},3\text{-endo-H}}$ 7.9 and $J_{3\text{-endo-H},4\text{-H}}$ ~ 0 Hz), the C^{2}-endo-H as a doublet centred at δ 3.23 ppm ($J_{2\text{-endo-H},3\text{-endo-H}}$ 7.9 Hz). The $C^{8}H_3$, $C^{10}H_3$ and $C^{9}H_3$ exhibited singlets at δ 1.35, 0.99 and 0.93 ppm respectively.

Hydroboration of 2-phenylbornylene (72) followed by equilibration at 160° and alkaline hydrogen peroxide oxidation gave, along with a trace of starting material (72; 0.2%), an increased amount of 3-exo-hydroxy-2-endo-phenylbornane (96). The equilibration reaction carried out at 160° showed that the 3-exo-borane intermediate is thermodynamically more stable than the 3-endo-borane intermediate. The two hydroboration

reactions are summarised in Fig.28.

Hydroboration of 2-phenylbornylene (72) at 20° gave the ratio of endo- to exo-attack as 5:4 compared to the ratio for apobornylene (76) of 4:1[66]. This is taken as indicative of the intervention of torsional effects in controlling the stereochemistry of attack in the hydroboration of 2-phenylbornylene.

LAH reduction of the 2-endo- and 2-exo-phenylketones (87 and 88) gave the products resulting from attack at the exo- and endo-faces respectively.



N indicates product derived from endo-attack

X indicates product derived from exo-attack

Fig. 28.

Preparation of the cis-2-Phenylbornan-2,3-diols (59 and 92)

Reaction of osmium tetroxide[67] and potassium permanganate[68] with olefins provides a convenient route to cis-diols. Due to the prohibitive cost of osmium tetroxide the large scale cis-hydroxylation was carried out with alkaline potassium permanganate[68]. The reaction pathway (Fig.29) elucidated by Wiberg and Saegebarth[68] shows that the further transformation of intermediate I has two available pathways (a) and (b) leading to ketols and diols respectively (Fig.29.).

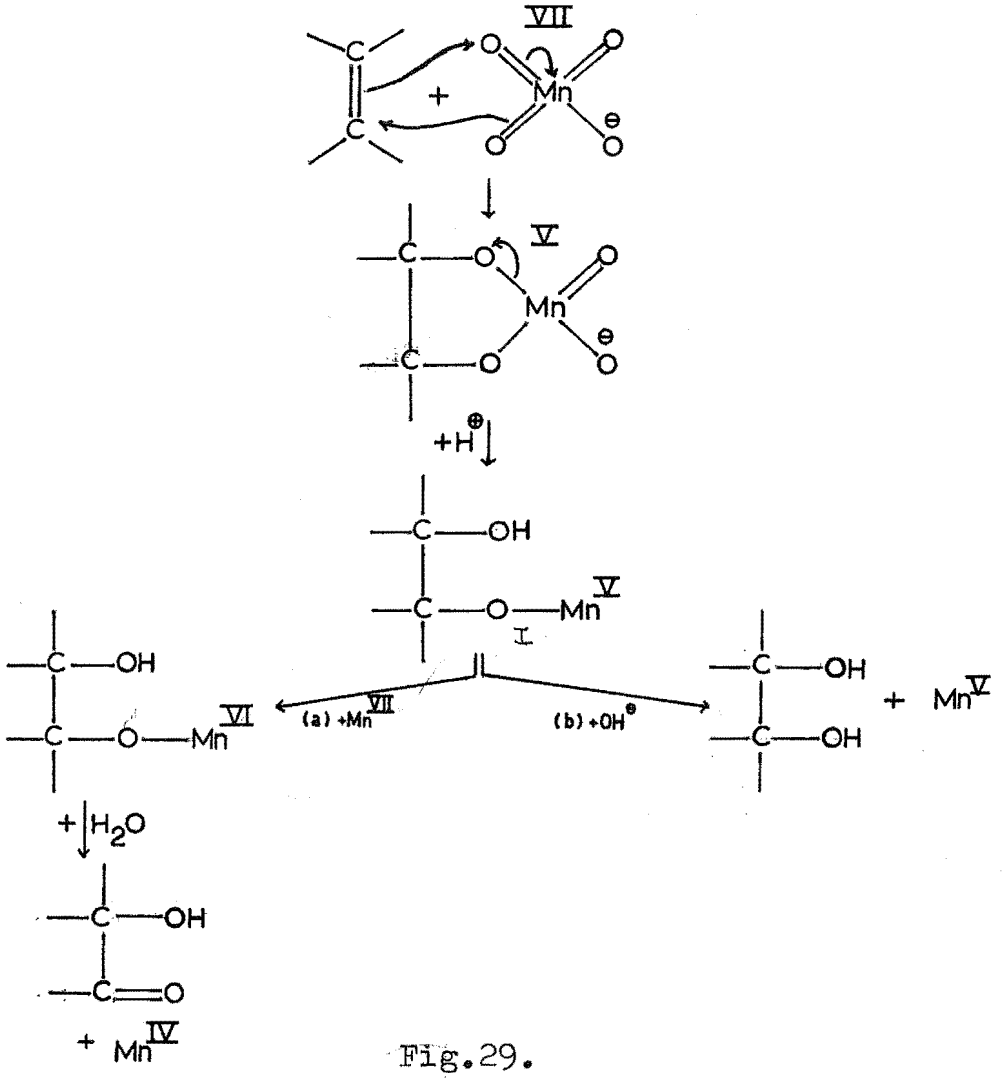


Fig.29.

Oxidation of 2-phenylbornylene (72; 21.2 g) with alkaline potassium permanganate[68] at 5-10° gave a neutral fraction along with a small amount of an acid fraction (1.80 g). Separation of the products, including starting material (72; 24%), present in the neutral fraction was accomplished *via* chromatography on activated and 10% deactivated alumina.

The product of slightly lower Rf compared with the starting material was identified as 7-keto-1-phenylcamphene (71) on the following evidence. The IR spectrum showed absorptions at 1779 cm^{-1} (C=O)[69] and 880 cm^{-1} (exocyclic methylene). The NMR spectrum exhibited the C^2 exocyclic methylene as singlets at δ 4.85 and 4.36 ppm and the C^{3}-*endo*-Me and C^{3}-*exo*-Me at δ 1.34 and 1.19 ppm. The ORD (*a* = +82.8) is consistent with the absolute stereochemistry of (+)-7-keto-1-phenylcamphene (71) as a result of the dominant effect of the unsaturated chromophore (Fig.30.)[70].

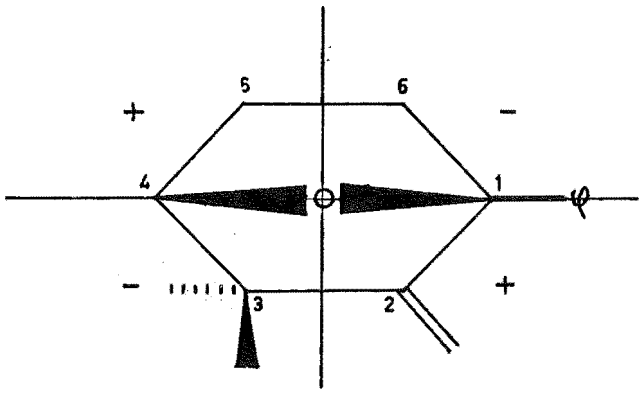


Fig.30.

Reduction of this ketone (71) with LAH gave the 7-*syn*-

hydroxyl-1-phenylcamphene (68) while Na-EtOH gave both the 7-syn- and 7-anti-hydroxy-1-phenylcamphene (68) and (69) in the ratio 1:4 separable by chromatography on activated alumina. The 7-syn-hydroxy-1-phenylcamphene structure (68) followed from the NMR spectrum which exhibited the C^2 exocyclic methylene at δ 4.88 and 4.54 ppm, the $C^{7\text{-anti-}}H$ as a quartet at δ 4.17 ppm ($J_{7\text{-syn-}OH,7\text{-anti-}H}$ 4.7 and $J_{4\text{-}H,7\text{-anti-}H}$ 1.4 Hz[61]) and the $C^{3\text{-exo-}}Me$ and $C^{3\text{-endo-}}Me$ at δ 1.42 and 1.21 ppm respectively. The IR spectrum showed absorptions at 3578 cm^{-1} (OH) and 880 cm^{-1} (exocyclic methylene). The 7-syn-hydroxyl configuration of 68 follows from the LAH reduction occurring from the least hindered face and the NMR spectrum which shows the $C^{3\text{-exo-}}Me$ deshielded by 0.21 ppm relative to the $C^{3\text{-endo-}}Me$ (cf. $C^{19}Me$ deshielded by 0.225 ppm by a 6βOH in steroids[64]). The 7-anti-hydroxyl-1-phenylcamphene structure (69) follows from the NMR spectrum which exhibited the C^2 exocyclic methylene at δ 4.64 and 4.18 ppm, the $C^{7\text{-syn-}}H$ as a broad doublet at δ 4.54 ppm ($W_{h/2}$ 4 Hz, $J_{4\text{-}H,7\text{-syn-}H} > 0$ Hz[61]) and the C^3 gem-dimethyl as a singlet at δ 1.15 ppm. The IR spectrum showed absorptions at 3599 cm^{-1} (OH) and 890 cm^{-1} (exocyclic methylene). The 7-anti-hydroxyl configuration of 69 follows from the NMR which shows the $C^{3\text{-exo-}}Me$ deshielded by 0.00 ppm relative to the $C^{3\text{-endo-}}Me$ (cf. $C^{19}Me$ deshielded by -0.008 ppm by a 6αOH in steroids[64]) and the method used to reduce the ketone (71)[69,71]. The epimeric nature of these alcohols (68 and 69) was proved by their CrO_3-pyridine oxidation to the parent ketone (71).

The 7-keto-1-phenylcamphene (71) presumably arises via a Wagner-Meerwein rearrangement (Fig.31).

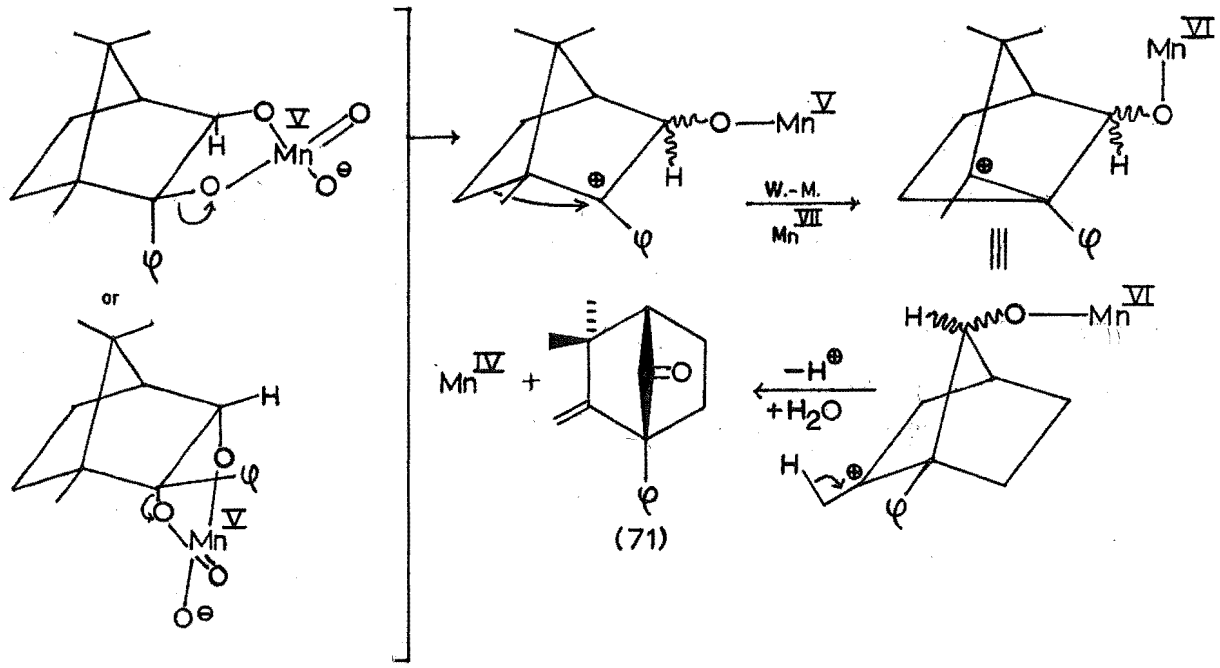


Fig.31.

A trace of a second ketone (0.3%) was also found which was identical with 2-endo-phenylbornan-3-one (87). A possible mechanism for its formation involves a 2,3-exo-hydride shift (Fig.32.).

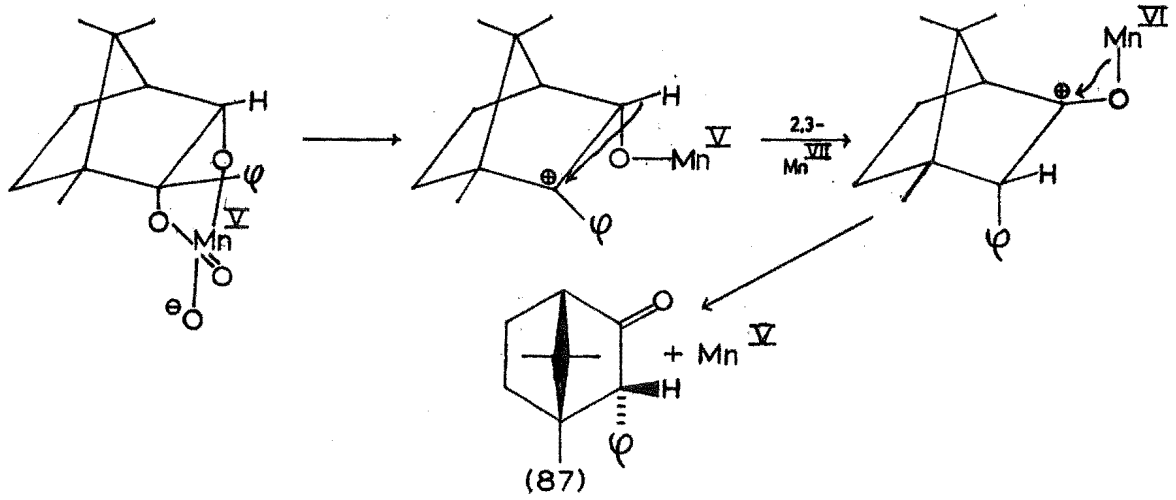


Fig.32.

The next major product eluted was an alcohol (2%) identical to 7-syn-hydroxy-1-phenylcamphene (68). This product is considered to be the result of a Wagner-Meerwein rearrangement (Fig.33.).

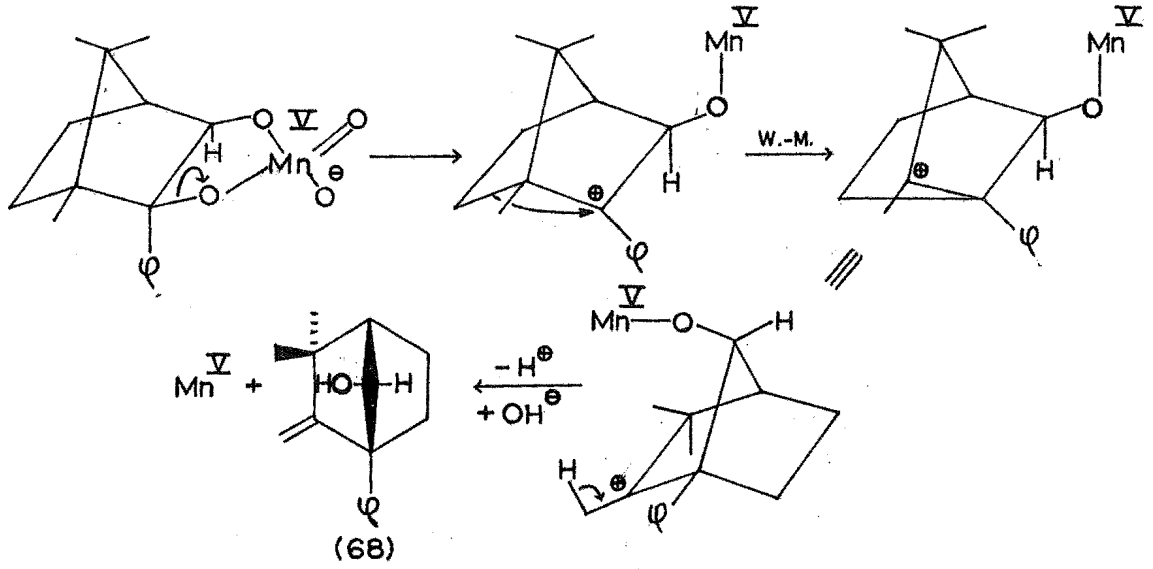


Fig.33.

Also isolated by chromatography in a 2% yield was 2-exo-hydroxy-2-endo-phenylbornan-3-one (58). The IR spectrum showed absorptions at 3550 cm^{-1} (OH) and 1750 cm^{-1} (C=O). The NMR spectrum exhibited the C^4H as a doublet centred at δ 2.37 ppm ($J_{4-H,5-exo-H}$ 4.2 Hz) and the C^8H_3, $C^{10}H_3$ and C^9H_3 as singlets at δ 1.24, 1.15 and 1.02 ppm respectively. The ORD of the ketol showed a molecular amplitude, a = -24.2.

The stereochemistry at C^2 was established by CrO_3-pyridine oxidation of the cis-exo-diol (59) which afforded the ketol (58; 63%) and by LAH reduction of this ketol (58) to give two diols (59 and 94) separable by chromatography on activated alumina. The cis-exo-diol (59, 12%) was identical to an authentic sample (see p.49). The other diol isolated in a 57% yield was identified as 2-exo,3-endo-dihydroxy-2-endo-phenylbornane (94). The IR spectrum showed absorptions at 3612 cm^{-1} (OH) while the NMR spectrum exhibited the $C^{3-exo-}H$ as a quartet centred at δ 4.38 ppm ($J_{3-exo-H,4-H}$ 4.4 and $J_{3-exo-H,5-exo-H}$ 0.9 Hz), the $C^{2-exo-}OH$ and $C^{3-endo-}OH$ as a broad signal centred at δ 2.28 ppm ($W_{h/2}$ 8 Hz) along with the C^8H_3, C^9H_3 and $C^{10}H_3$ as singlets at δ 1.23, 0.93 and 0.74 ppm. Both the IR and NMR are consistent with the assigned structure. The cis:trans diol ratio is explicable on the basis of the directing influence of the 2-exo-hydroxyl function (Fig.34.) and the severe steric hindrance imposed on the endo-face by the phenyl substituent.

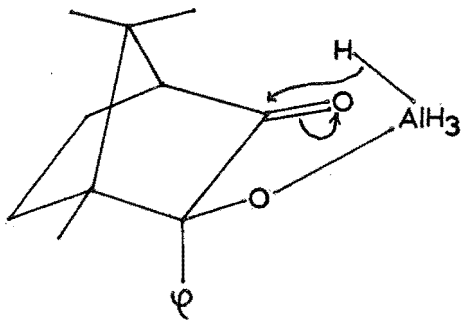


Fig.34.

A second ketol 2-endo-hydroxy-2-exo-phenylbornan-3-one (57) was also isolated in an 8% yield. The structure follows from the IR spectrum which showed absorptions at 3550 and 3460 cm^{-1} (OH) and 1748 cm^{-1} (C=O) while the NMR exhibited the C^4H as a doublet centred at δ 2.40 ppm ($J_{4-H,5-exo-H}$ 4.0 Hz) and the $C^{10}H_3$, C^9H_3 and C^8H_3 as singlets at δ 1.14, 0.98 and 0.82 ppm. The ORD spectrum showed a molecular amplitude a = -24.2.

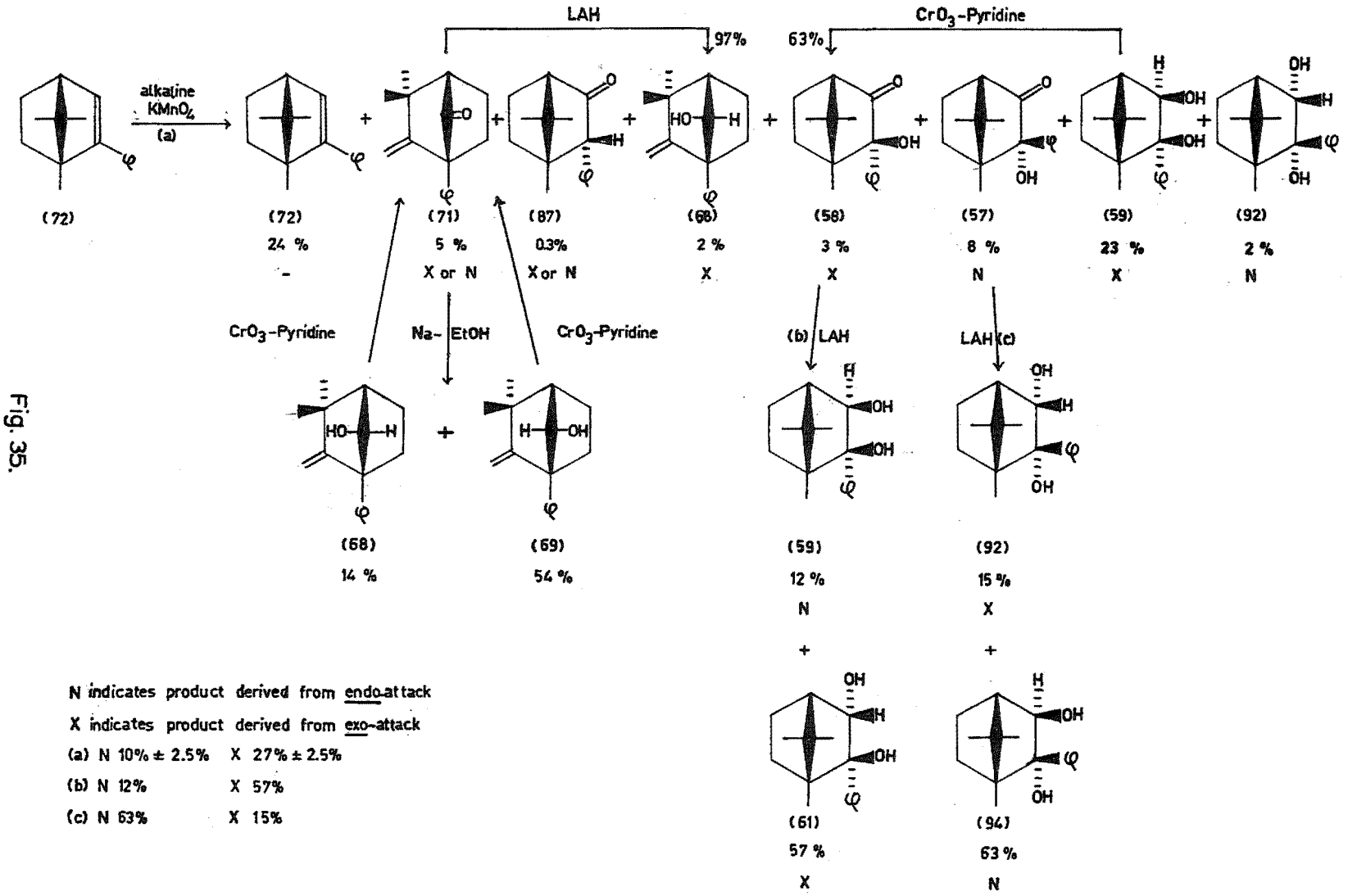
The stereochemistry at C^2 was established by LAH reduction of the ketol (57) to give the diols (61 and 92) separable by crystallization and chromatography on activated alumina. The major product, the trans-diol (92) is a result of the directing influence of the 2-endo-hydroxyl function (cf. Fig.34.) and the steric hindrance imposed on the exo-face by the 2-exo-phenyl substituent and the C^7 gem-dimethyl. The cis-endo-diol (61; 15%) was identical to an authentic sample (see p.49).

The two ketols (58 and 57) are presumed to arise by $KMnO_4$ oxidation of the hydroxy manganese (V) ester (Fig.29.).

The seventh product isolated in 23% yield from the $KMnO_4$-2-phenylbornylene reaction was the 2-exo,3-exo-dihydroxy-2-endo-phenylbornane (59). The cis-nature of the diol is based on the known cis-dihydroxylation of olefins by $KMnO_4$. The NMR spectrum of the diol (59) exhibited the $C^{3\text{-endo-}}H$ as a singlet at δ 4.29 ppm ($J_{3\text{-endo-}H,4\text{-}H} \sim 0$ Hz) hence determining the C^3OH configuration. The $C^{2\text{-exo-}}OH$ and $C^{3\text{-exo-}}OH$ were shown as a broad signal centred at δ 2.87 ppm ($W_{h/2}$ 10 Hz), the C^4H as a doublet centred at δ 1.85 ppm ($J_{4\text{-}H,5\text{-exo-}H}$ 3.9 Hz) along with the C^8H_3, $C^{10}H_3$ and C^9H_3 as singlets at δ 1.31, 0.92 and 0.87 ppm respectively. The IR spectrum showed an absorption at 3595 and 3510 cm^{-1} (OH).

The final product isolated in 2% yield by chromatography on 10% deactivated alumina was assigned the 2-endo,3-endo-dihydroxy-2-exo-phenylbornane structure (92) on the following evidence. The known cis-dihydroxylation of olefins by $KMnO_4$ and the NMR spectrum which exhibited the $C^{3\text{-exo-}}H$ as a doublet centred at δ 4.89 ppm ($J_{3\text{-exo-}H,4\text{-}H}$ 4.0 Hz) provided evidence for the configuration at C^2 and C^3. The $C^{2\text{-endo-}}OH$ and $C^{3\text{-endo-}}OH$ were shown as a broad signal centred at δ 2.49 ppm ($W_{h/2}$ 12 Hz), the C^8H_3 and $C^{10}H_3$ at δ 0.90 ppm and the C^9H_3 at δ 0.72 ppm.

In conclusion $KMnO_4$ oxidation of 2-phenylbornylene (Fig.35.) gives a complex mixture of "normal" $KMnO_4$ oxidation products (58, 57, 59 and 92) along with three



N indicates product derived from endo-attack

X indicates product derived from exo-attack

(a) N 10% ± 2.5% X 27% ± 2.5%

(b) N 12% X 57%

(c) N 63% X 15%

Fig. 35.

products resulting from rearrangement (71, 87 and 68). The proportion of products resulting from exo- and endo-attack by $KMnO_4$ is estimated at 27%±2.5% and 10%±2.5% respectively. In the $KMnO_4$ oxidation of norbornylene (73) only the exo-diol (104) is found[68] which is presumably due to the exo-face being sterically less hindered.

Preparation of 2,3-Oxygenated-2-phenylbornanes (49, 50 and 95)

Treatment of diol monotosylates with base normally results in rearrangement. In the base catalysed rearrangement of the vic.-diol monotosylate (105)[72] the pinane reacts in an "up conformation" which places the C^1-C^2 bond in a planar relationship with the departing tosylate group (Fig.36.) to give the ketone (106). In the "down conformation" the product would be the ketone (107).

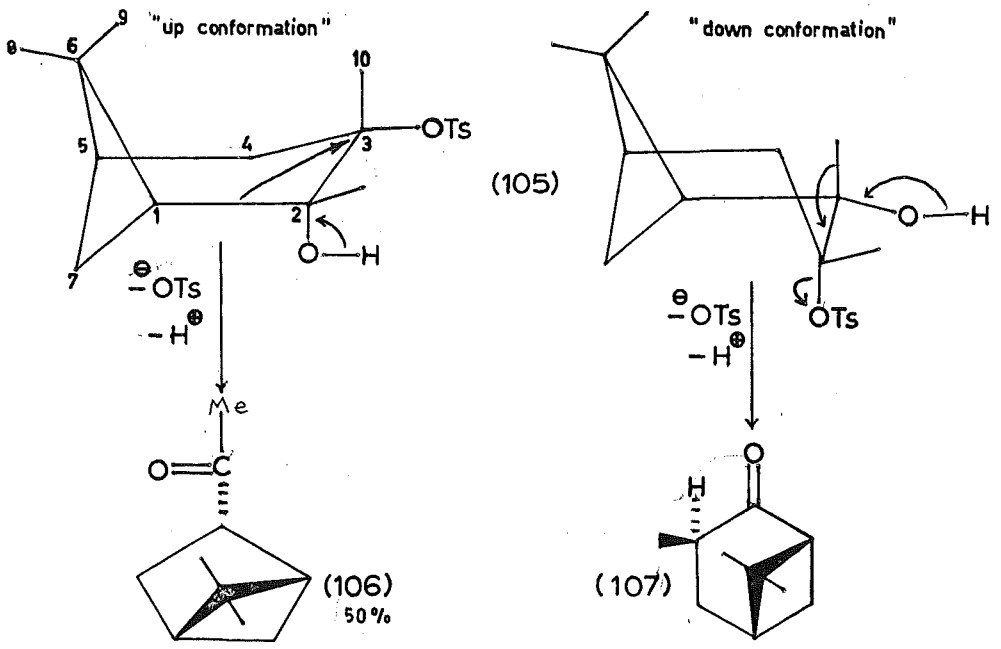


Fig.36.

No planar syn-1,2-diol monotosylates have been studied.

Reaction of the 2-exo-hydroxy-3-exo-tosylate (60) for 15 min with t.-BuOK-t.-BuOH at 70° gave the unstable 2,3-exo-epoxy-2-phenylbornane (49). This product was identified by its NMR spectrum which exhibited the C^{3}-endo-H as a doublet centred at δ 3.39 ppm ($J_{3\text{-endo-H},4\text{-H}}$ 1.3 Hz), the $C^{4}H$ as a broad signal centred at δ 2.13 ppm ($W_{h/2}$ 6 Hz) along with the $C^{8}H_3$, $C^{10}H_3$ and $C^{9}H_3$ as singlets at δ 1.25, 1.02 and 0.84 ppm respectively. The $C^{8}H_3$ at δ 1.25 ppm is assigned on the basis of deshielding by the epoxide ring and the 2-endo-phenyl substituent. The IR spectrum which showed no absorptions due to (OH) or (C=O) was consistent with this structure.

The 2-endo-hydroxy-3-endo-tosylate (93) was prepared by reacting the cis-endo-diol (92) with p-tolylsulphonyl chloride. This product was identified by its IR spectrum which showed absorptions at 3587, 3523 cm^{-1} (OH), 1373, 1189 and 1177 cm^{-1} ($-O-SO_2-$) and the NMR spectrum which exhibited the C^{3}-exo-H as a doublet centred at δ 5.66 ppm ($J_{3\text{-exo-H},4\text{-H}}$ 4.6 Hz), the tolyl-Me as a singlet at δ 2.43 ppm along with the $C^{9}H_3$, $C^{10}H_3$ and $C^{8}H_3$ as singlets at δ 0.88, 0.82 and 0.77 ppm.

Reaction of this tosylate (93) for 15 min with t.BuOK-t.-BuOH at 70° gave a mixture shown by NMR and IR to consist of 2-endo-phenylbornan-3-one (87) and the unstable 2,3-endo-epoxy-2-phenylbornane (50) in the ratio 11:6. The endo-epoxide (50) was identified by its NMR spectrum which exhibited a doublet centred at δ 3.83 ppm ($J_{3\text{-exo-H},4\text{-H}}$ 3.3 Hz), the $C^{10}H_3$ at δ

1.27 ppm and the C^8H_3 and C^9H_3 at δ 0.85 and 0.83 ppm.

Reaction of the cis-exo-diol (59) with $SOCl_2$-pyridine gave the 2,3-cis-exo-dihydroxy-2-phenylbornane cyclic sulphites (95a and 95b; 7:3) (cf.[26]). Crystallization from ether gave the predominant cyclic sulphite isomer (95a) with an elemental analysis corresponding to the molecular formula $C_{16}H_{20}O_2S$. The NMR spectrum showed the $C^{3\text{-endo-}}H$ as a singlet at δ 5.35 ppm ($J_{3\text{-endo-}H,4\text{-}H} \sim 0$ Hz), the C^4H as a doublet centred at δ 2.31 ppm ($J_{4\text{-}H,5\text{-exo-}H}$ 5.1 Hz) and the C^8H_3, $C^{10}H_3$ and C^9H_3 as singlets at δ 1.14, 1.01 and 0.93 ppm respectively. The IR spectrum showed absorptions at 1216, 968, 945 and 906 cm^{-1} (-O-SO-O-) consistent with a cyclic sulphite. The IR and NMR spectra for the other cyclic sulphite isomer (95b) were obtained by inference from the IR and NMR spectra of a mixture of the cyclic sulphites (95a and 95b; 3:4). The NMR spectrum showed the $C^{3\text{-endo-}}H$ as a singlet at δ 4.85 ppm ($J_{3\text{-endo-}H,4\text{-}H} \sim 0$ Hz), the C^4H as a doublet centred at δ 2.32 ppm ($J_{5\text{-exo-}H,4\text{-}H}$ 5.1 Hz) and the C^8H_3, $C^{10}H_3$ and C^9H_3 as singlets at δ 1.50, 1.00 and 0.96 ppm respectively.

Assignment of the anti-configuration to the S=O for the major cyclic sulphite isomer (95a) is based on the NMR spectrum which shows the C^8H_3 in the syn-cyclic sulphite (95b) is deshielded (ca. 0.36 ppm) relative to the C^8H_3 in the anti-cyclic sulphite (95a) (cf. the pinane cyclic sulphites (38a and 38b)[73]).

Preparation of 2,3-Oxygenated butanes (108, 109, 116 and 117)

cis- and trans-2,3-Epoxybutanes (108 and 109) and butan-2,3-diol cyclic sulphites (116 and 117) were prepared as simple systems in order to study the acid and thermal catalysed rearrangements.

The preparation of cis- and trans-2,3-epoxybutanes (108 and 109) was accomplished by the preparation of a mixture of cis- and trans-but-2-ene from butan-1-ol and sulphuric acid[74]. Reaction of the mixture of cis- and trans-but-2-ene with calcium hypochlorite gave the D,L-threo- and D,L-erythro-2,3-butane chlorohydrins (110 and 111) respectively as a mixture[74]. Elimination of HCl with KOH then gave a mixture of cis- and trans-2,3-epoxybutane (108 and 109; 3:7; 52%) respectively[74]. Separation of the two epoxides (108 and 109) was effected by spinning band distillation.

The preparation of pure D,L- and meso-butan-2,3-diol cyclic sulphites (116 and 117) was effected by the separation of technical butan-2,3-diol (113 and 114; 1:1) by spinning band distillation to give pure D,L- and meso-butan-2,3-diols (113) and (115). The D,L- and meso-butan-2,3-diols (113) and (115) on treatment with $SOCl_2$ gave the D,L-amphi-butan-2,3-diol cyclic sulphite (116) and a mixture of meso-anti- and meso-syn-butan-2,3-diol cyclic sulphites (117a and 117b; 7:2) respectively (cf.[27,73,75-77]).

A partial separation of the meso-anti- and meso-syn-cyclic sulphites by preparative GLC gave a mixture of 117a and 117b in

the ratio 13:1. By comparison of the NMR spectra of the two different mixtures the NMR of the anti-isomer (117a) showed the C^2H and C^3H as a multiplet centred at δ 4.92 ppm and the C^2Me and C^3Me at δ 1.32, 1.29, 1.24 and 1.22 ppm. The syn-isomer (115b) exhibited the C^2H and C^3H as a multiplet centred at δ 4.53 ppm and the C^2Me and C^3Me at δ 1.55, 1.52, 1.47 and 1.44 ppm.

The assignment of the anti-configuration of the S=O relative to the methyls for isomer 117a and the syn-configuration to isomer 117b relies on the deshielding effect of the S=O (Fig.37.) (cf. the pinane cyclic sulphites[27,73] and the 2,3-cis-exo-dihydroxy-2-phenylbornane cyclic sulphites p.53).

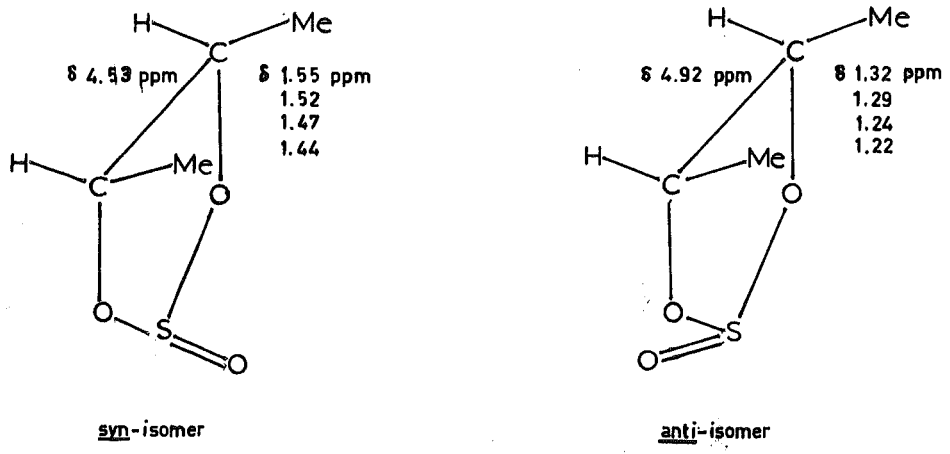
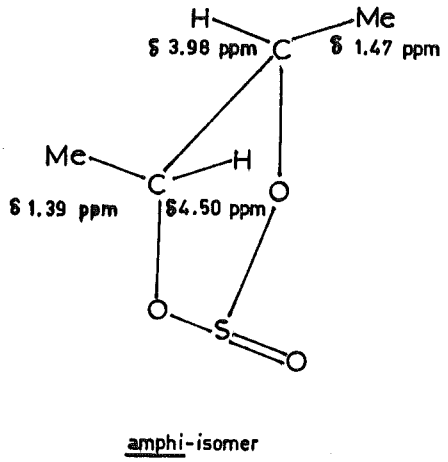


Fig.37.

Here the C^2H and C^3H for isomer 117a are deshielded by ca. 0.39 ppm relative to the C^2H and C^3H for isomer 117b while the C^2Me and C^3Me for isomer 117b are deshielded by ca. 0.23 ppm relative to the C^2Me and C^3Me of isomer 117a.

The NMR spectrum of the D,L-amphi-cyclic sulphite (116) showed the syn-H as a multiplet centred at δ 4.50 ppm, the anti-H as a multiplet centred at δ 3.98 ppm, the syn-Me as a doublet centred at δ 1.47 ppm and the anti-Me as a doublet centred at δ 1.39 ppm.

In this cyclic sulphite (116) the syn-H relative to the anti-H is deshielded by ca. 0.52 ppm and the syn-Me relative to the anti-Me is deshielded by ca. 0.08 ppm consistent with the known deshielding effect of the S=O (Fig.38.).



amphi-isomer

Fig.38.

Rearrangements of 2,3-Oxygenated-2-phenylbornanes (49, 50 and 95)

The mixture of 2-endo-phenylbornan-3-one (87; 64%) and 2,3-endo-epoxy-2-phenylbornane (50; 36%) on treatment with m-chloroperbenzoic acid in $CDCl_3$ gave rearrangement to the 2-endo-phenylbornan-3-one (87) envisaged as arising by a 3,2-hydride migration.

The unstable 2,3-exo-epoxide rearranged spontaneously at 20° within 24 hr to give a mixture from which three products could be isolated by chromatography on activated alumina.

The major product isolated in 67% yield was identified as the ring opened aldehyde (119) on the basis of its UV spectrum which showed an absorption at λ_{max} 233 nm (ϵ 5860)[78] and its IR spectrum which showed absorptions at 2713 and 1721 cm^{-1} (CHO). The NMR spectrum exhibited the C^1CHO as a singlet at δ 9.98 ppm, the C^3 vinyl-Me as a narrow multiplet centred at δ 1.52 ppm ($W_{h/2}$ 4 Hz) and the C^2 gem-dimethyl as singlets at δ 1.30 and 1.17 ppm. This product readily underwent auto-oxidation to the corresponding acid (120) identified by its IR spectrum which showed absorptions at 2980 cm^{-1} ($W_{h/2}$ 380 cm^{-1}; CO_2H) and 1698 cm^{-1} (C=O). The NMR spectrum exhibited the C^1CO_2H as a broad signal centred at δ 9.97 ppm ($W_{h/2}$ 15 Hz) which disappeared on addition of D_2O, the C^3 vinyl-Me as a narrow multiplet centred at δ 1.52 ppm ($W_{h/2}$ 3 Hz) and the C^2 gem-dimethyl as singlets at δ 1.30 and 1.19 ppm. The UV spectrum showed an absorption at λ_{max} 231 nm (ϵ 4100) characteristic of substituted styrenes[78].

The minor components were identified as 2-endo-phenyl-bornan-3-one (87; 2%) and 7-syn-hydroxy-1-phenylcamphene (68; 24%) identical to authentic samples.

The NMR of the crude mixture from the spontaneous rearrangement of 2,3-exo-epoxy-2-phenylbornane (49) showed the main products were the ring opened aldehyde (119; 74%) and

7-syn-hydroxy-1-phenylcamphene (68; 26%) with only a trace of any ketones (consistent with the IR of the crude mixture).

Rearrangement of the exo-epoxide (49) with m-chloroperbenzoic acid in $CDCl_3$ gave four main products after 1 hr. The NMR spectrum of the crude product mixture enabled the relative yields and identity of the various products to be assigned.

The products of rearrangement were the ring opened aldehyde (119; 61%), 7-syn-hydroxy-1-phenylcamphene (68; 8%), 2-endo-phenylbornan-3-one (87; 23%) along with 2-exo-phenylbornan-3-one (88; 8%). A control experiment with 2-exo-phenylbornan-3-one (88) under identical reaction conditions showed no sign of epimerisation to the C^2 epimeric ketone (87) indicating that the 2-endo-phenylbornan-3-one (87; 23%) is not formed by equilibration and must therefore be considered as a primary product of the reaction.

The endo-phenyl ketone is thought to result from kinetically controlled exo-protonation of the enol (Fig.39.)[60] while the exo-phenyl ketone (88) presumably arises via 3,2-hydride migration.

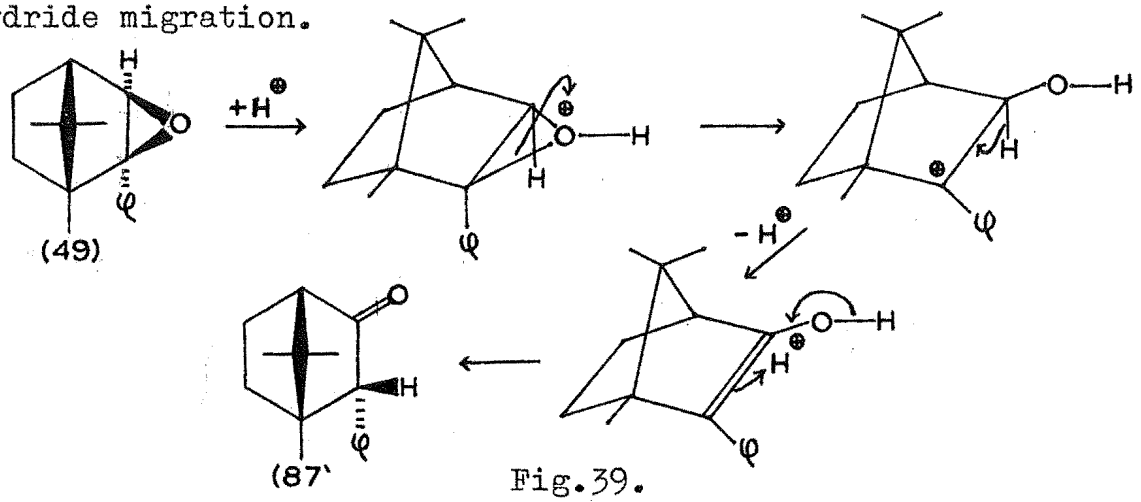


Fig.39.

The most probable mechanism for the formation of the ring opened aldehyde (119) and the 7-syn-hydroxy-1-phenylcamphene (68) involves an initial Wagner-Meerwein rearrangement as shown in Fig.40. followed by fragmentation or proton loss.

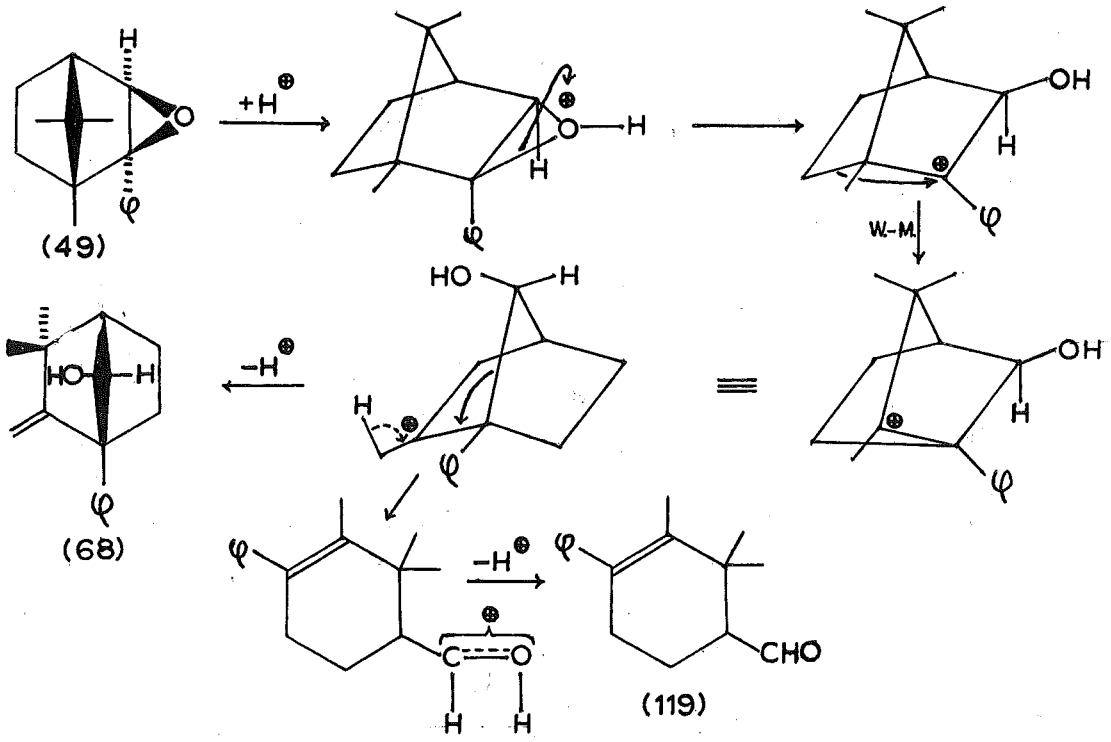


Fig.40.

In the Lewis acid catalysed rearrangement of 2,3-endo-epoxybornane (103) the ring opened aldehyde (118) is formed[79]. This product is analogous to that formed from the acid-catalysed rearrangement of the 2,3-exo-epoxy-2-phenylbornane (49). However it is in contrast to the acid catalysed rearrangement of 2,3-endo-epoxy-2-phenylbornane (50) which gives no ring opened aldehyde (119). This is probably a reflection of the greater stability of a tertiary carbonium ion

with respect to the carbonium ion formed from the 2,3-endo-epoxybornane (103).

Pyrolysis of a mixture of the cyclic sulphites (95a and 95b; 4:5) at 300° for 30 min gave a mixture of products. Separation by chromatography on alumina gave in order of elution, a complex mixture of hydrocarbons, the ring opened aldehyde (119; 72%) and 2-endo-phenylbornan-3-one (87; 24%). Similar treatment of a mixture of cyclic sulphites (95a and 95b; 4:5) and analysis by NMR showed the presence of the aldehyde (119) and the ketone (87) in the ratio 3:1 while the pure cyclic sulphite (95a) gave the ratio as 2:1. A control reaction with 2-exo-phenylbornan-3-one (88) along with a trace of the pure anti-cyclic sulphite (95a) gave the C^2 epimeric ketone (87) showing that the 2-exo-phenylketone epimerises under the reaction conditions. The ring opened aldehyde is considered to be formed via a Wagner-Meerwein rearrangement followed by fragmentation. The preferential formation of the 2-exo-phenylketone (87) from the cyclic sulphite (95a) could be a reflection of the ease of the S-$O^{\ominus}$ abstracting the C^{3}-endo-proton with formation of an enol intermediate (Fig.41.) followed by preferred exo-protonation[60].

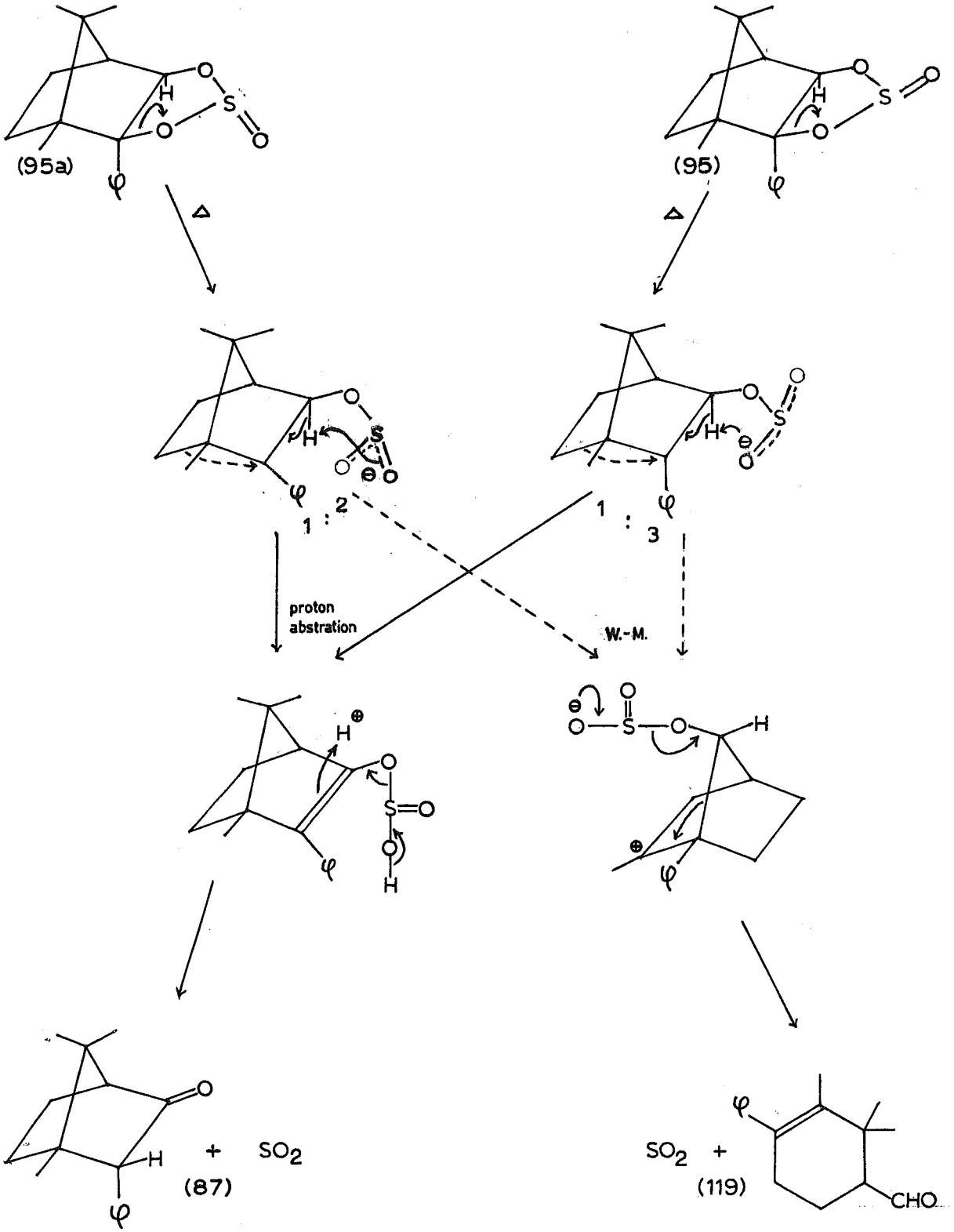


Fig.41.

Rearrangements of 2,3-Oxygenated butanes (108, 109, 116 and 117)[80]

Pyrolysis of the meso-cyclic sulphite mixture (117a and 117b; 7:2) in the gas phase at 400° gave essentially a quantitative yield of butan-2-one containing only a trace (< 1%) of isobutyraldehyde. Similar treatment of the D,L-cyclic sulphite (116) gave a mixture (9:1) of butan-2-one and isobutyraldehyde in addition to some unreacted cyclic sulphite (116; 5%)[80] (Table.5. p.63). The reaction of cis- and trans-2,3-epoxybutanes (108 and 109) with $MgBr_2$ are reported[81] to give only butan-2-one (75% and 62% yield respectively). In contrast the cis-epoxide (108) with BF_3-etherate in ether soln gave[82] butan-2-one (13%) while the trans-epoxide (109) gave a mixture (10:1.8; total yield 12%) of butan-2-one and isobutyraldehyde. These yields were based on the estimated compositions of 2,4-dinitrophenylhydrazone mixtures formed from the crude reaction products. Reaction of 2,3-epoxybutanes (108 and 109) with BF_3-etherate in ether as determined by Swallow[80] gave a reaction mixture, the composition of which was determined by GLC. While the yields of carbonyl containing compounds from both isomers were similar (60%) the cis-isomer (108) gave only butan-2-one while the trans-isomer (109) gave a mixture of butan-2-one and isobutyraldehyde in the ratio ca. 3:1. Similar product ratios have been reported[83] for the aq. phosphoric acid catalysed rearrangements of 2,3-epoxybutanes (108 and 109) and the butan-2,3-diols (113 and 115). The trans-epoxide (109) and meso-butan-2,3-diol (115) gave mixtures of butan-2-one and

Table.5.

The Product Yields (Molar Percentages) for the Pyrolysis of the 2,3-Epoxybutanes (108 and 109) in the Presence of SO_2 and the 2,3-Butane cyclic sulphites (116 and 117)

Conditions	Cyclic sulphite $-N_2$-glass		Epoxide $-N_2$-glass		Epoxide $-SO_2$-glass		Epoxide $-N_2$ or SO_2- SE-30 coated glass	
	Isomer							
Product	trans-	cis-	trans-	cis-	trans-	cis-	trans-	cis-
Starting material	5		54	66	1	27		
Epimer of starting material				2			Total	
Butan-2-one	86	100	9	16	19	43		
Isobutyraldehyde	9	trace < 1	14	5	11	9	reaction	
n-Butyraldehyde				2				
But-1-en-3-ol (125)			23	9	26	16	in all	
amphi-dioxolane (122)							cases	
anti-dioxolane (121a)								
syn-dioxolane (121b)				43[a]			< 5%	

a The yields of the syn-dioxolane (121b), isobutyraldehyde and unreacted epoxide (109) were not reproduceable. However if the formation of the syn-dioxolane (121b) in the trap via reaction of the unreacted epoxide and isobutyraldehyde is taken into account then the yields of isobutyraldehyde and unreacted epoxide are reproduceable to ±5% of the quoted values.

isobutyraldehyde in the ratio *ca.* 3:1, while the *cis*-epoxide (108) and D,L-butan-2,3-diol (113) gave essentially pure butan-2-one contaminated with traces of isobutyraldehyde (1-6%). However the factors determining the differing ratios of butan-2-one and isobutyraldehyde arrising from these various rearrangements are at present unknown.

It has been reported in the literature[84-87] that a number of epoxides condense with sulphur dioxide at various temperatures and pressure and in certain cases in the presence of catalysts to give the corresponding cyclic sulphite. For this reason the pyrolysis of the *cis*- and *trans*-epoxides at 400° in an atmosphere of SO_2 were carried out over glass and SE-30 coated glass. Control experiments in an atmosphere of N_2 were also carried out. The results are summarised in Table. 5. Analysis of the product mixtures were performed using GLC and NMR comparison with authentic samples.

The reaction of the epoxides at 400° with SO_2 over SE-30 coated glass gave no significant amounts of rearranged products and no cyclic sulphite.

The reactions over glass, after taking into account the loss of epoxide and isobutyraldehyde *via* *syn*-dioxolane formation, showed no significant differences. The higher rearrangement product yields in the presence of SO_2 compared to N_2 however may be indicative of greater catalysis due to SO_2 activation of the glass surface. No definite conclusions could be drawn.

The presence of but-1-en-3-ol (125) in the crude products was confirmed by isolation *via* preparative GLC and by NMR and GLC comparison with an authentic sample.

The isobutyraldehyde formed in the *trans*-epoxide-SO_2-glass reaction condenses with the unreacted *trans*-epoxide in the presence of SO_2 to give the *meso*-*syn*-dioxolane (121b). Isolation by preparative GLC gave a mixture of *meso*-*anti*- and *meso*-*syn*-dioxolanes (121a and 121b; 3:1) with physical data consistent with that reported[88]. The acid catalysed reaction of *meso*-butan-2,3-diol (115) with isobutyraldehyde gave an authentic mixture of the *meso*-dioxolanes (121a and 121b; 1:2; 33%).

It is known that aldehydes and epoxides in the presence of acid catalysts (H_2SO_4 and BF_3-etherate) can give rise to dioxolanes[88]. However the mechanism for its formation was in doubt. Recently Yandovoskii and Temnikova[90] had suggested a mechanism for its formation from epoxides and carbonyl compounds under Lewis acid catalysis (Fig.42.).

Evidence to support this mechanism has now been provided by reaction of *cis*- and *trans*-butane epoxides (108 and 109) with acetone-^{18}O in the presence of BF_3-etherate which were shown[81] to give the *meso*- and D,L-2,2,4,5-tetramethyl-1,3-dioxolanes (123 and 124) respectively. The dioxolane structures were confirmed by preparation of *meso*- and D,L-dioxolanes (123 and 124) by acid catalysed reaction of acetone with *meso*-butan-2,3-diol (115) and D,L-butan-2,3-diol (113)[91].

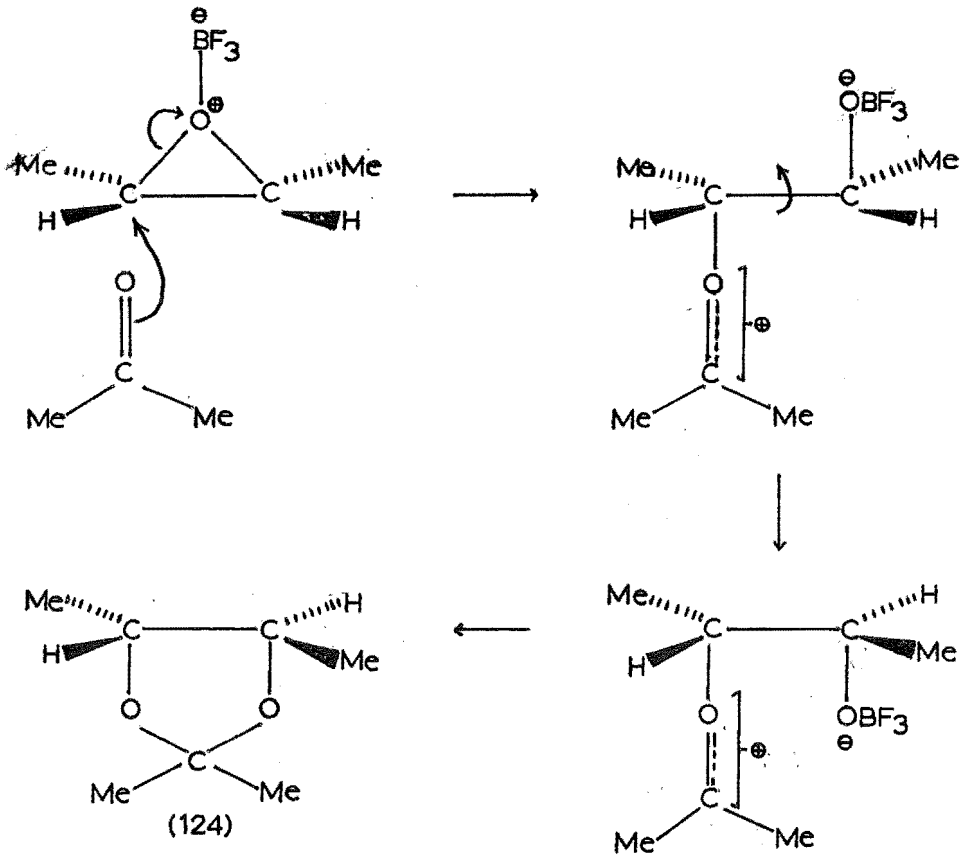


Fig.42.

APPENDIX A

"Abnormal" Oxymercuration Products from Olefins[92]

The vinyl mercury acetate (81) is considered to arise by loss of the C^3 proton from the mercurinium ion (79) (see p.20) in constrast to the normal products found for the reactions of norbornylene (73)[41], apobornylene (76)[41], 1-methylnorbornylene (74)[41], 4-methylbornylene (78)[42] and 2-phenylbornylene (75)[43].

In order to define the factors responsible for the abnormal reaction the mercuration of a series of compounds, 1,1-diphenylethylene (126), bornylene (77), camphene (130) and β-pinene (139) were studied.

1,1-Diphenylethylene (126), camphene (130) and β-pinene (139) were commercially available. Bornylene (77) was prepared in a 47% yield by reaction of camphene benzenesulphonylhydrazone (134) with LiMe[93].

1,1-Diphenylethylene (126) reacted normally giving the hydroxy mercury acetate (127) identified by its IR spectrum which showed an absorption at 3370 cm^{-1} (OH) and an absorption at 1582 cm^{-1} (HgOAc). The NMR spectrum exhibited the C^1 diphenyl as a multiplet centred at δ 7.27 ppm ($W_{h/2}$ 16 Hz), the C^1OH as a broad signal centred at δ 3.76 ppm ($W_{h/2}$ 13 Hz), the C^2H_2 as a singlet at δ 2.85 ppm with satellites centred at δ 2.85 ppm ($J_{2-H,^{199}Hg}$ 204.4 Hz[46]) and the acetate as a singlet at δ 1.85 ppm. Treatment with aq. NaCl gave the hydroxy

mercury chloride (128) with consequent loss of the acetate absorption in the IR and the acetate signal in the NMR. The structural assignment of the hydroxy mercury acetate (127) was confirmed by its $NaBH_4$ reduction which gave 1,1-diphenylethan-1-ol (129) identical to an authentic sample.

Oxymercuration of camphene (130) followed by $NaBH_4$ reduction gave a mixture from which the normal product camphene hydrate (131) could be isolated as the major component. Identification followed from comparison with an authentic sample. Preferential sublimation of camphene hydrate (131) from this mixture gave a residue from which di-(2-exo-hydroxy-camphanyl) mercury (132) was isolated by crystallization. The structure (132) followed from an accurate mass measurement of the parent ion peak in the mass spectra; the IR spectrum which showed an absorption at 3360 cm^{-1} (OH); LAH reduction of the dialkyl mercury (132) to camphene hydrate (131) and the NMR spectrum of 132 which exhibited the C^{2}-exo-OH as a singlet at δ 1.92 ppm, the $-CH_2-Hg-CH_2-$ as a singlet at δ 1.29 ppm and the C^{3}-exo-Me and C^{3}-endo-Me as singlets at δ 1.00 and 0.92 ppm respectively. An attempted chromatographic separation on 5% deactivated alumina of the crude reaction mixture from which the dialkyl mercury (132) could not be eluted, gave in addition to camphene hydrate (131) a low yield of four isomeric divinyl mercury compounds (133). The structure (133) is consistent with an accurate mass measurement of the parent ion in the mass

spectra, the IR spectrum and the UV spectrum which showed an absorption at λ_{max} 237 nm (ϵ 15400). The NMR spectrum exhibited the olefinic protons as signals centred at δ 6.26, 5.78 and 5.50 ppm along with the gem-dimethyl as singlets at δ 1.25 and 1.18 ppm. Since no trace of the divinyl mercury (133) could be detected in the NMR spectrum of the crude reaction mixture, it is considered to arise from the dialkyl mercury (132) by dehydration during chromatography.

Oxymercuration of bornylene (77) gave a material which showed no signals in the NMR spectrum charateristic of olefinic protons. In situ demercuration of this material gave a mixture consisting of seven components (GLC). Chromatography on activated alumina afforded a mixture of isobornyl acetate (136; 10%) and epiisobornyl acetate (138; 9%) followed by isoborneol (135; 36%) and epiisoborneol (137; 27%). The mixture of isobornyl acetate (136) and epiisobornyl acetate (138) was identified by comparison with authentic isobornyl acetate (136). The NMR spectrum of epiisobornyl acetate (138) by inference showed the $C^{3\text{-endo-}}H$ as a quartet centred at δ 4.49 ppm ($J^{app.}_{2\text{-endo-}H,3\text{-endo-}H}$ 6.8 and $J^{app.}_{2\text{-exo-}H,3\text{-endo-}H}$ 4.9 Hz), the $C^{3\text{-exo-}}OAc$ as a singlet at δ 1.98 ppm along with the $C^{8}H_3$, $C^{10}H_3$ and $C^{9}H_3$ as singlets at δ 1.02, 0.90 and 0.88 ppm respectively. Confirmation of the nature of the acetates was obtained by LAH reduction which gave isoborneol (135) and epiisoborneol (137). Epiisoborneol was identified by comparison

of its physical data (m.p., $[\alpha]_D$, IR) with the literature values[94]. The structure (137) was confirmed by its NMR spectrum which showed the C^3-endo-H as a quartet centred at δ 3.83 ppm ($J^{app.}_{2\text{-endo-H},3\text{-endo-H}}$ 6.8 and $J^{app.}_{2\text{-exo-H},3\text{-endo-H}}$ 4.9 Hz) and the C^8H_3, $C^{10}H_3$ and C^9H_3 as singlets at δ 1.35, 1.08 and 0.88 ppm respectively. Isoborneol (135) was identified by comparison with an authentic sample. The isolation of these acetates (136 and 138) from an oxymercuration reaction in aq. THF although unusual, may be rationalised in terms of internal collapse of a mercurinium ion - acetate ion - pair competing favourably with nucleophilic attack by water at the hindered C^2 and C^3 positions.

β-Pinene (139) on oxymercuration gave a crude product shown by NMR to be a mixture (7:2) of two unstable alkenyl mercury acetates (140 and 142). The assigned structures (140 and 142) followed from the IR spectrum which showed an absorption at 1603 cm^{-1} (HgOAc) and the UV spectrum which showed absorptions at λ_{max} 203 nm (ϵ 9390) and 245 nm (ϵ 8130). The NMR spectrum exhibited the C^3H as a broad signal at δ 5.33 ppm and the $C^{10}H$ as a broad signal at δ 4.99 ppm in the ratio 7:2, the -CH_2-Hg-OAc of 140 as a multiplet centred at δ 2.75 ppm, the acetates as a singlet at δ 2.01 ppm along with the C^9H_3 and $C^{10}H_3$ of 140 as singlets at δ 1.29 and 0.89 ppm respectively. Treatment with aq. NaCl gave a mixture of two unstable alkenyl mercury chlorides (141 and 143; 7:2 by NMR). The assigned

structures (141 and 143) followed from accurate mass measurement of the parent ion peak in the mass spectra and the NMR and IR spectra which showed the absence of an acetate. In situ $NaBH_4$ reduction of these alkenyl mercurys gave a complex mixture containing β-pinene (139) and various dimeric compounds (144) in ratio ca. 1:2.7 (GLC). The main dimer peak in the GLC was isolated by preparative GLC. The NMR spectrum which exhibited signals due to olefinic protons at δ 5.20 and 4.52 along with a number of methyl signals showed it to be a mixture. The UV spectrum showed an absorption at λ_{max} 215 nm (ε 10900) while the accurate mass measurement of the parent ion peak in the mass spectra and elemental analysis were consistent with the dimer formulation.

From this study oxymercuration of an olefin which gives rise to a mercurinium ion (79) may either react with a nucleophile, H_2O, AcOH, MeOH, $AcO^{\ominus}$ to give "normal" oxymercuration products or lose a proton to give alkenyl mercury acetates. The alkenyl mercury acetates have only been isolated as primary products from the oxymercuration of 2-phenylbornylene (72) and β-pinene (139). The other olefins have yielded normal oxymercuration products. These results suggest that proton loss occurs where the potential carbonium ion is abnormally shielded from external nucleophilic attack (Fig.43.). The formation of dimers on demercuration of the alkenyl mercury acetate (140 and 142) and the divinyl mercury (80) on partial demercuration of

the vinyl mercury acetate (81) supports the suggestion[46] of radical intermediacy (Fig.19.).

APPENDIX B

NMR Spectra of Bicyclic Monoterpenes

(a). The Variation of Coupling Constants with Dihedral Angle

Coupling constants (J) between two vicinal protons on adjacent sp^3 hybridized carbon atoms and their variation with dihedral angle (Φ) has been subject to valence bond computations by Karplus[95] who has given the equation relating the two variables as:

$$J = \begin{cases} 8.5\cos^2\Phi - 0.28 & 0^\circ \leq \Phi \leq 90^\circ \\ 9.5\cos^2\Phi - 0.28 & 90^\circ \leq \Phi \leq 180^\circ. \end{cases}$$

He subsequently showed[96] that a more accurate representation was:

$$J = 4.22 - 0.5\cos\Phi - 4.5\cos 2\Phi.$$

On the basis of a number of substituted norbornanes and norbornenes Laszlo and Schleyer[61] have shown the applicability of the Karplus $\{J,\Phi\}$ relationship and have given the coupling constants that are found between various protons in the norbornane and norbornene structures. The coupling constants of value to this work are tabulated in Table.6.

Subsequently Anet et al[97] has shown that the $J_{2\text{-}\underline{endo}\text{-}H,\ 3\text{-}\underline{endo}\text{-}H}$ in various substituted norbornenes is nearer 9.0 Hz (cf. 4.4 - 8.0 Hz stated by other workers[98,99]).

The values derived from this work including the

long range coupling constants observed are listed (Table.6.) and compare favourably with those tabulated.

Table.6.

Selected Coupling Constants found in Substituted Norbornanes and Norbornenes[61]

Protons	J (Hz)
2-exo-H,3-exo-H	7.5 - 8.2
2-exo-H,3-endo-H - 2-endo-H,3-exo-H	2.1 - 3.4
3-exo-H,4-H	3.2 - 3.9
3-endo-H,4-H	0
7-H,1-H - 7-H,4-H	1.5 - 2.0

Table.7.

Coupling Constants found in Substituted Bornanes

Protons	J (Hz)			
	Beckett[100]	Tori[101]	Anet[102]	This Work
2-exo-H,3-exo-H	9-9.5	9-10	8.9	9.9
2-endo-H,3-endo-H	7-7.8	7.4-7.9	7.7	6.8-7.9
2-exo-H,3-endo-H - 2-endo-H,3-exo-H	3.2-4.4	3.2-5.0	2.2-2.3	4.4-6.5
3-exo-H,4-H	3.4-4.7	3.2-4.5	ca.4.0-4.4	3.7-4.6
3-endo-H,4-H	0	0	0	0
Long range				
2-exo-H,6-exo-H	1-1.4	1-1.9	1.4	1.7-1.9
3-exo-H,5-exo-H	1-1.5	0.8-1.0	1.0	0.9-1.2

The increase in the coupling, $J_{2\text{-endo-H},3\text{-exo-H}}$, and the

decrease in the coupling, $J_{2\text{-endo-H},3\text{-endo-H}}$, for the bornane system in comparison to norbornane and norbornene systems is rationalized by Beckett[100] on the basis of steric interaction between substituents and the bridgehead gem-dimethyl. If the dihedral angle between the $C^{2\text{-endo-H}}$, $C^{3\text{-exo-H}}$ is greater than 120° (corresponding to J 2.1 Hz) then an increase in the coupling constant would be expected. Similarly if the dihedral angle between the $C^{2\text{-endo-H}}$, $C^{3\text{-endo-H}}$ is greater than 0° (corresponding to J 8.2 Hz) then a decrease in the coupling constant would be expected.

(b). Assignment of the Methyl Signals (Table.8. p.78)

In the NMR spectra of numerous terpenes having a gem-dimethyl and a lone tertiary methyl the lone methyl is usually of greater amplitude (lower $W_{h/2}$). Kumler[103] has suggested that this effect is due to decreased freedom of rotation of the gem-dimethyl relative to the lone tertiary methyl. However experimental evidence[104-106] now suggests that this broadening of the gem-dimethyl is directly attributable to spin-spin coupling between protons adopting a "W" configuration separated by 4σ bonds. On amplitude and line width of the methyl signals it is often possible to define the lone tertiary methyl in the NMR spectra. The remaining signals due to the gem-dimethyl may be assigned if the anisotropy or deshielding effect of various substituents are known. In this work knowledge of the anisotropy effects of C=O, C=C and the phenyl

substituent along with the deshielding effect of the cyclic sulphite, hydroxyl and halogen groups are required.

A detailed computer analysis by ApSimon et al[107,108] has shown that the anisotropies of the C=O and C=C can be represented as in Fig.43 in contrast to the "shielding cones" proposed in texts[109,110].

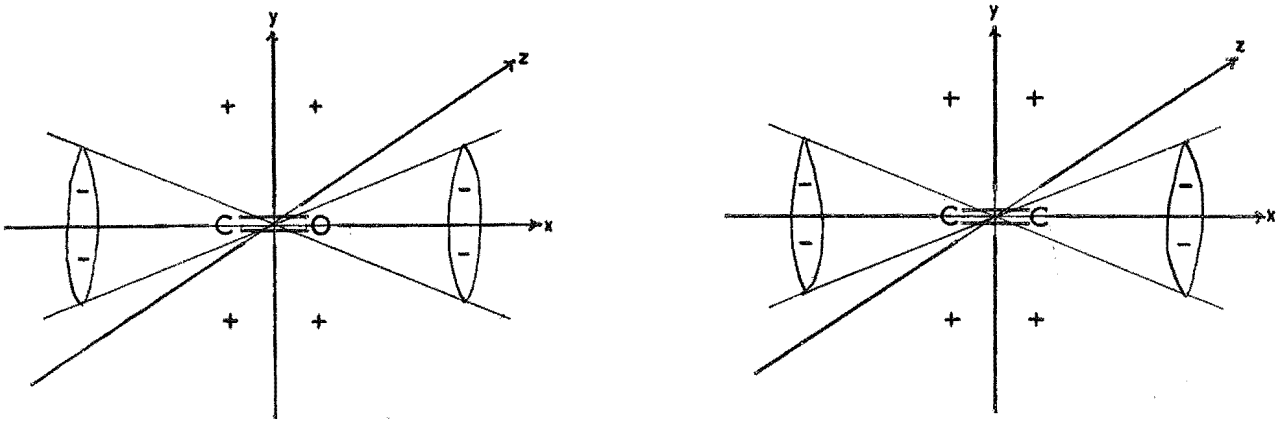


Fig.43.

In the case of the phenyl group the model proposed by Jackman[110] with a shielding cone perpendicular to the benzene ring was used (Fig.44a.). However the ability of the phenyl substituent to take up different conformations, probably with time-averaging of NMR signals, in various substituted phenyl-bornanes causes difficulty in interpretation of the NMR spectra.

The cyclic sulphites appear to have a deshielding cone perpendicular to the S=O plane[73] due to anisotropy and dipolar effects of the S=O (Fig.44b.).

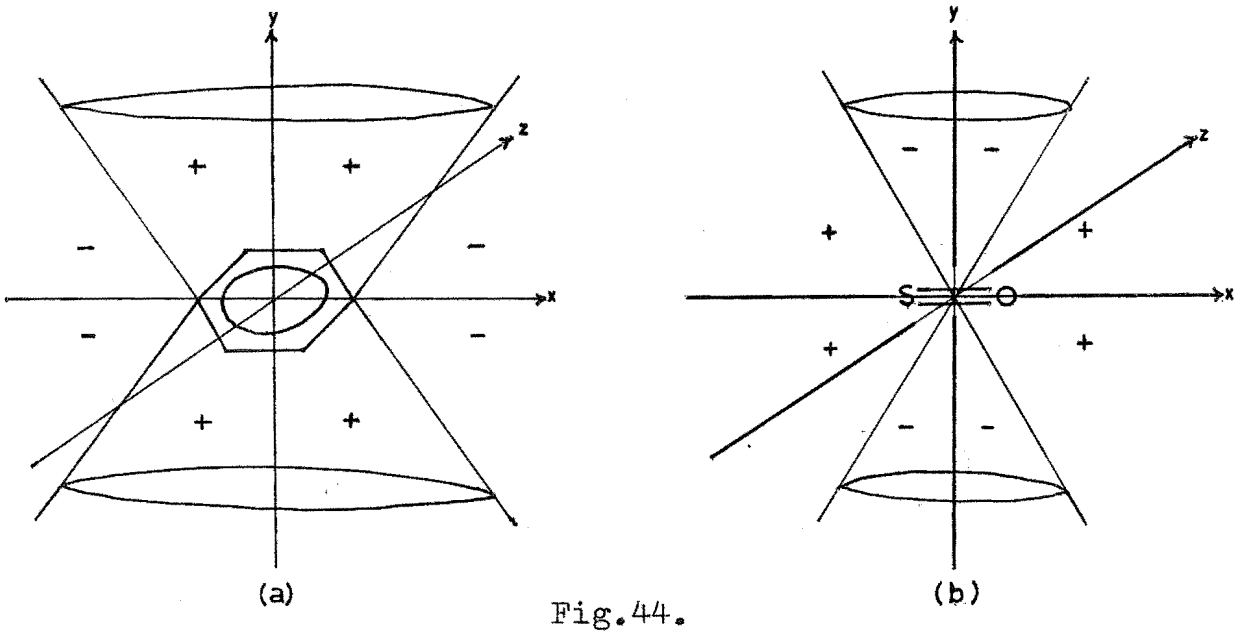


Fig.44.

Finally the deshielding effect of a hydroxyl or halogen group syn-diaxial to a methyl group is well known[64].

Use of these effects on a qualitative basis for various substituted bornanes has effectively allowed the assignment of the various methyls to particular signals in most of the NMR spectra. The NMR spectrum of 3-exo-hydroxy-2-exo-phenyl-(100) which exhibits three methyl signals at δ 1.35, 0.99 and 0.93 ppm will serve to illustrate. The singlet at δ 0.99 was assigned as the $C^{10}H_3$ on the basis of $W_{h/2}$ and its signal amplitude relative to the other two gem-dimethyl signals. The C^9H_3 is remote from the $C^{2\text{-exo-}}$phenyl and $C^{3\text{-exo-}}$OH and is unlikely to be deshielded markedly. The δ 0.93 ppm signal was therefore assigned to the C^9H_3. The remaining methyl at δ 1.35 ppm was assigned as the C^8H_3. This is the result of deshielding arising from the $C^{3\text{-exo-}}$OH along with additional deshielding arising from the $C^{2\text{-exo-}}$phenyl which has been

twisted away from the C^8H_3 as a result of steric interaction with the C^{3}-exo-OH.

Table.8.

NMR Spectra of Bicycloheptanes
(Methyl Assignments)

Bicycloheptanes	(ppm)		
Bornanes	C^8H_3	C^9H_3	$C^{10}H_3$
Bornylene (77)	0.77	0.83	1.03[a]
2-Phenylbornylene (72)	0.91	0.84	1.11[a]
2-Phenylborn-2-en-3-yl mercury acetate (81)	0.94	0.83	1.02[a]
Di-(2-phenylborn-2-en-3-yl) mercury (80)	0.78	0.84	0.99[a]
3,10-Dibromo-2-phenylbornylene (91)	1.18	1.03	-
Isoborneol (135)[b]	1.02	0.82	0.90[a]
Epiisoborneol (137)	1.08	0.83	0.88[a]
Isobornyl acetate (136)[b]	0.98	0.84	0.84
Epiisobornyl acetate (138)	1.02	0.88	0.90[a]
2-exo-Hydroxy-2-endo-phenylbornane (46)	1.27	0.92	0.92
3-exo-Hydroxy-2-endo-phenylbornane (96)	1.27	0.93	0.75[a]
3-exo-Hydroxy-2-exo-phenylbornane (100)	1.35	0.93	0.99[a]
3-endo-Hydroxy-2-endo-phenylbornane (99)	1.05	0.99	0.65[a]
3-endo-Hydroxy-2-exo-phenylbornane (98)	0.70	0.88	0.90[a]
2-exo,3-exo-Dihydroxy-2-endo-phenylbornane (59)	1.31	0.87	0.92[a]
2-exo,3-endo-Dihydroxy-2-endo-phenylbornane (94)	1.23	0.93	0.74[a]

Bornanes continued	C^8H_3	C^9H_3	$C^{10}H_3$
2-endo,3-endo-Dihydroxy-2-exo-phenylbornane (92)	0.72	0.90	0.90
2-endo,3-exo-Dihydroxy-2-exo-phenylbornane (61)	1.10	0.97	1.14[a]
2-exo-Hydroxy-2-endo-phenyl-3-exo-p-tosyloxybornane (60)	1.34	0.87	0.87
2-endo-Hydroxy-2-exo-phenyl-3-endo-p-tosyloxybornane (93)	0.77	0.88	0.82[a]
2-endo-Hydroxy-2-exo-phenyl-3-exo-p-tosyloxybornane (62)	1.08	0.98	1.16[a]
2-exo-Hydroxy-2-endo-phenylbornan-3-one (58)	1.24	1.02	1.15[a]
2-endo-Hydroxy-2-exo-phenylbornan-3-one (57)	0.82	0.98	1.14[a]
2-endo-Cyclohex-1'-en-1'-yl 3-exo-hydroxybornane (97)	1.14	0.83	0.83
2,3-exo-Epoxy-2-endo-phenylbornane (49)	1.25	0.84	1.02[a]
2,3-endo-Epoxy-2-exo-phenylbornane (50)	0.83 or 0.85	0.85 or 0.83	1.27[a]
anti-2-exo,3-exo-Dihydroxy-2-endo-phenylbornane cyclic sulphite (95a)	1.14	0.93	1.01[a]
syn-2-exo,3-exo-Dihydroxy-2-endo-phenylbornane cyclic sulphite (95b)	1.50	0.96	1.00[a]
Camphor benzenesulphonylhydrazone (134)	0.49	0.85	1.08[a]
Tricyclenes	C^8H_3	C^9H_3	$C^{10}H_3$
3-exo-Hydroxy-2-phenyltricyclene (89)	1.03	0.92	0.83[a]

Pinanes	C^8H_3	C^9H_3	$C^{10}H_3$
α-Pinene-10-yl mercury acetate (140)	1.29	0.89	-
α-Pinene-10-yl mercury chloride (141)	1.30	0.89	-

Camphanes	C^{3}-exo-Me	C^{3}-endo-Me	C^2Me
Camphene hydrate (131)	0.99	0.90	1.22[a]
Di-(2-exo-hydroxycamphanyl)-mercury (132)	1.00	0.92	-
1-Phenylcamphene exo-epoxide (85)	1.04	0.90	-
7-syn-Hydroxy-1-phenylcamphene exo-epoxide (86)	1.27	1.01	-

Camphenes	C^{3}-exo-Me	C^{3}-endo-Me
1-Phenylcamphene (66)	1.14	1.14
7-anti-Bromo-1-phenylcamphene (70)	1.24	1.20
7-anti-Hydroxy-1-phenylcamphene (69)	1.15	1.15
7-syn-Hydroxy-1-phenylcamphene (68)	1.42	1.21
7-Keto-1-phenylcamphene (71)	1.19	1.34

Substituted Norbornanes	C^{2}-exo-Me	C^{2}-endo-Me	C^1Me
7-syn-Hydroxy-7-anti-phenyl-1,2,2-trimethylnorbornane (65)	1.22	1.00	1.07[a]

All NMR spectra were recorded in 10% w/v $CDCl_3$ solns.

[a] Methyl signal of greatest amplitude and smallest $W_{h/2}$ (if not superimposed) relative to the gem-dimethyl signals.

[b] See reference 101.

EXPERIMENTAL

Melting points measured in sealed capillaries are uncorrected. Optical rotations were determined for $CHCl_3$ solns in a 10 mm quartz cell on an ETL - NPL Automatic Polarimeter. ORD curves were recorded for cyclohexane solns at 20° in a 10 mm quartz cell (1 mm indicated) on a JASCO Optical Rotatory Dispersion Recorder Model ORD/UV-5. Infra-red spectra were recorded on a Perkin-Elmer 337 for ca. 0.025 M CS_2 solns in a 1 mm NaCl cell. Spectra recorded for smears, nujol mulls or KBr discs are indicated. Ultra-violet absorptions were determined for cyclohexane solns in a 1 mm quartz cell on a Shimadzu MPS-50L. NMR spectra were recorded for 10% w/v $CDCl_3$ solns with TMS as an internal standard on a Varian A-60 spectrometer with a Varian Model V-6058A spin decoupler. Calibration of each NMR spectrum was accomplished by addition of $CHCl_3$ to the sample after the spectrum had been recorded. NMR spectra for other solvents and other concentrations are indicated. Analytical GLCs were recorded on a Varian Aerograph 1200 with a flame ionization detector. Preparative GLCs were carried out on a Aerograph Autoprep 705 with a flame ionization detector. Micro-analyses were determined at the University of Otago. Mass spectra were recorded on an AEI Model M.S.9 spectrometer with a $M/\Delta M = 15000$.

The alumina used for column chromatography was P. Spence, Grade H, activated, or 5% or 10% deactivated, prepared by

addition of 5% v/v or 10% v/v of 10% aq HOAc respectively. The silica gel used for column chromatography was Crosfield quality grade B.S.S. Sorbsil. All solvents for column chromatography were technical grade. Benzene was distilled off P_2O_5.

Merck silica gel G with binder and Fluka alumina type H were used for TLC. Benzene, $CHCl_3$ and $CHCl_3$-acetone mixtures were the solvents most commonly used for developing the chromatograms. The visualizing agents used were iodine, phosphomolybdic acid in EtOH, or $SbCl_3$ in $CHCl_3$.

D-(-)-2-exo-Hydroxy-2-endo-phenylbornane (46)[29]

(a). Bromobenzene (235 g) in ether (350 ml) was added to Mg (37.5 g) in ether (650 ml) over 2 hr with stirring. A soln of D-(+)-camphor (188 g) in ether (250 ml) was then added over 30 min. After stirring at 20° for 16 hr saturated aq. NH_4Cl was added. Isolation by means of ether gave a crude product (237 g). Biphenyl and unreacted D-(+)camphor were removed by steam distillation in the presence of $NaHCO_3$. Isolation by means of ether gave D-(-)-2-exo-hydroxy-2-endo-phenylbornane (46; 67.2 g, 24%) which crystallized on standing.

Recrystallization from n-pentane gave massive prisms, m.p. 41-42°, $[\alpha]_D^{25}$ -34° (c 0.99), ν_{max} 3600, 757, 699 cm^{-1}; λ_{max} 243 (shoulder, ϵ 168), 248 (ϵ 215), 253 (ϵ 262), 259 (ϵ 299), 265 nm (ϵ 226); NMR δ 7.45 ($W_{h/2}$ 13 Hz; C^{2}-endo-phenyl); 1.81 (C^{2}-exo-OH); 1.27 ($C^{8}H_3$); 0.92 ppm ($C^{9}H_3$ and $C^{10}H_3$): (Found: C, 83.2; H, 9.7. $C_{16}H_{22}O$ requires: C, 83.4; H, 9.6%).

(lit.[29,31]: m.p. 57.6-58.5° and 59-60.5°).

(b). Same as (a). except the crude product (8.60 g) was adsorbed onto activated alumina (250 g).

Elution with n-pentane gave a mixture of D-(-)-2-phenyl-bornylene (72; 52 mg, 0.5%), (-)-1-phenylcamphene (66; 22 mg, 0.2%) and biphenyl (180 mg, 4%) as estimated by NMR and GLC* using samples of pure hydrocarbons for comparison.

n-Pentane-benzene (19:1) and (9:1) eluted D-(+)-camphor

(43; 3.66 g - some loss due to its high vapour pressure) as crystals (sublimed), m.p. and m.m.p. 175-176°, $[\alpha]_D^{25}$ -43° (c 1.10), identical (IR, GLC*, NMR, TLC) with an authentic sample.

n-Pentane-benzene (3:1) and (1:1) gave D-(-)-2-exo-hydroxy-2-endo-phenylbornane (46; 3.17 g, 27%) as massive prisms (n-pentane), m.p. and m.m.p. 41-42°, identical (IR, NMR, TLC) with the previous sample.

* GLC at 150° on a 5' 10% PEG 1500 on Chromosorb P HMDS 60/80# column.

D-(-)-2-endo-Hydroxy-2-exo-phenyl-3-exo-p-tolylsulphonyloxy-bornane (62)

p-Tolylsulphonyl chloride (331 mg) was added to D-(-)-2-endo,3-exo-dihydroxy-2-exo-phenylbornane (61; 331 mg) in pyridine (2 ml) and kept at 20° for 14 days. Isolation by means of ether gave a crude product (529 mg) which was adsorbed onto 10% decativated alumina.

Elution with n-pentane-benzene (1:1) gave D-(-)-2-endo-hydroxy-2-exo-phenyl-3-exo-p-tolylsulphonyloxybornane (62; 471 mg, 88%) as crystals (n-pentane), m.p. ca. 84-88°, $[\alpha]_D^{26}$ ca. -8° (c 0.21), ν_{max} 3598, 1370, 1190, 1178, 812, 769, 706 cm^{-1}; λ_{max} ca. 252 (inflexion, ϵ 650), 259 (inflexion, ϵ 602) 261 (inflexion, ϵ 580), 265 (inflexion, ϵ 510), 267 (inflexion, ϵ 473), 273 nm (ϵ 325): NMR doublet centred at δ 7.53 ($J_{ortho\text{-}H, meta\text{-}H}$ 7.1 Hz; tolyl-ortho-H); 7.20 ($W_{h/2}$ 10 Hz; tolyl-meta-H

and C^{2}-exo-phenyl); 4.63 (C^{3}-endo-H); 2.27 (tolyl-Me); 1.16 ($C^{10}H_3$); 1.08 ($C^{8}H_3$); 0.98 ppm ($C^{9}H_3$): (Found: C, 69.0; H, 6.8; S, 7.6. $C_{23}H_{28}O_4S$ requires: C, 69.0; H, 7.1; S, 8.0%).

D-(+)-2-exo-Hydroxy-2-endo-phenyl-3-exo-p-tolylsulphonyloxybornane (60)

p-Tolysulphonyl chloride (6.00 g) was added to D-(-)-2-exo,3-exo-dihydroxy-2-endo-phenylbornane (59; 3.00 g) in pyridine (15 ml) and kept at 20° for 30 days. Isolation by means of ether gave a crude product (5.11 g) which was adsorbed onto 10% deactivated alumina (50 g).

Elution with n-pentane-benzene (1:1) gave D-(+)-2-exo-hydroxy-2-endo-phenyl-3-exo-p-tolylsulphonyloxybornane (60; 4.62 g, 95%) as needles (n-pentane), m.p. 90-91°, $[\alpha]_D^{26}$ -28° (c 1.07), ν_{max} 3586, 3518, 1373, 1189, 1176, 812, 764, 701 cm^{-1}; λ_{max} 253 (inflexion, ϵ 528), 258 (inflexion, ϵ 590), 260 (ϵ 655), 262 (ϵ 679), 265 (ϵ 664), 267 (ϵ 613), 273 nm (shoulder, ϵ 464): NMR δ 7.66 ($J_{ortho\text{-}H,meta\text{-}H}$ 8.6 Hz; tolyl-ortho-H); 7.31, 7.33 (C^{2}-endo-phenyl); 7.21 ($J_{ortho\text{-}H,meta\text{-}H}$ 8.6 Hz; tolyl-meta-H); 5.04 (C^{3}-endo-H); 2.39 (tolyl-Me); 1.34 ($C^{8}H_3$); 0.87 ppm ($C^{9}H_3$ and $C^{10}H_3$): (Found: C, 69.2; H, 7.3; S, 8.1. $C_{23}H_{28}O_4S$ requires: C, 69.0; H, 7.1; S, 8.0%).

LAH reduction of D-(-)-2-endo-hydroxy-2-exo-phenyl-3-exo-p-tolysulphonyloxybornane (62)

LAH (200 mg) was added to a soln of the tosylate (62; 115

mg) in ether (10 ml) and heated under reflux for 2 hr. Decomposition of excess LAH by addition of $Na_2SO_4.10H_2O$ followed by an aq. soln of sodium potassium tartrate and isolation by means of ether gave a terpenoid mixture (64 mg).

Adsorption onto activated alumina (5 g) and elution with n-pentane-benzene (1:1) gave D-(-)-3-endo-hydroxy-2-endo-phenylbornane (99; 20 mg, 30%) as crystals (n-pentane), m.p. and m.m.p. 92-93°, identical (IR, NMR, TLC) with an authentic sample. Minor traces of six other compounds were found two before elution and four after elution of D-(-)-3-endo-hydroxy-2-endo-phenylbornane (99).

LAH reduction of D-(+)-2-exo-hydroxy-2-endo-phenyl-3-exo-p-tolylsulphonyloxybornane (60)

LAH (200 mg) was added to a soln of the tosylate (60; 100 mg) in ether (10 ml) and heated under reflux for 2 hr. Decomposition of excess LAH by addition of $Na_2SO_4.10H_2O$ followed by an aq. soln of sodium potassium tartrate and isolation by means of ether gave a terpenoid mixture (54 mg) containing one major compound and traces of four minor compounds (TLC).

Adsorption onto activated alumina (5 g) and elution with n-pentane-benzene (1:1) gave 7-syn-hydroxy-7-anti-phenylmethyl-camphenilane (65; 25 mg, 43%) as an oil, $[\alpha]_D^{26}$ -21° (c 0.93), ν_{max} 3603, 755, 704 cm^{-1}; λ_{max} 243 (inflexion, ϵ 359), 249 (inflexion, ϵ 443), 253 (ϵ 515), 259 (ϵ 571), 265 nm (ϵ 527):

NMR δ 7.36 ($W_{h/2}$ 16 Hz; C^{7}-anti-phenyl); 1.49 (C^{7}-syn-OH); 1.22 (C^{2}-exo-Me); 1.07 (C^{1}Me); 1.00 ppm (C^{2}-endo-Me): M^{+} 230.167001 ($C_{16}H_{22}O$ requires 230.167061), (Found: C, 83.7; H, 9.6. $C_{16}H_{22}O$ requires: C, 83.4; H, 9.6%).

D-(-)-2-Phenylborn-2-en-3-yl mercury acetate (81)[39]

$Hg(OAc)_2$ (6.38 g) was added to a soln of D-(-)-2-phenylbornylene (72; 2.15 g) in aq. THF (20 ml; 1:1) and the mixture stirred at 20° for 7 days. Isolation by means of ether gave D-(-)-2-phenylborn-2-en-3-yl mercury acetate (81; 4.22 g, 88%) as a gum, n_D^{24} 1.5829, $[\alpha]_D^{23}$ -14° (c 1.10), ν_{max} (smear) 1601, (CS_2) 1300, 764, 700 cm^{-1}; λ_{max} 221 (inflexion, ε 10700), 265 nm (ε 7710): NMR δ 7.29 (C^{2}phenyl); 2.49 ($J_{4\text{-}H,5\text{-}exo\text{-}H}$ 3.0 Hz; $C^{4}H$); 1.98 ($C^{3}HgOAc$); 1.02 ($C^{10}H_3$); 0.94 ($C^{8}H_3$); 0.83 ppm ($C^{9}H_3$): RD (c 0.20), 1 mm cell; $[\Phi]_{275}$ 0°; $[\Phi]_{288}$ -2140° (trough); $[\Phi]_{300}$ -880°; $[\Phi]_{325}$ -269°; $[\Phi]_{350}$ -129°; $[\Phi]_{400}$ 0°: M^{+} (for ^{202}Hg) 470.130321 ($C_{18}H_{22}HgO_2$ requires 470.130297), (Found: C, 46.7; H, 4.7. $C_{18}H_{22}HgO_2$ requires: C, 45.9; H, 4.7%).

$NaBH_4$ reduction of D-(-)-2-phenylborn-2-en-3-yl mercuric acetate (81)[39]

(a). In aq. THF. A soln (0.5 M) of $NaBH_4$ in aq. NaOH (10 ml; 3M) was added to the vinyl mercury acetate (81; 2.14 g) in THF (10 ml) and aq. NaOH (20 ml; 1.5 M) and the mixture stirred at 20° for 10 min. Isolation by means of ether gave a mixture (1.20 g) consisting of D-(-)-2-phenylbornylene (72; 230

mg, 24%) and (-)-di-(D-2-phenylborn-2-en-3-yl)-mercury (80; 970 mg, 69%). The product composition was estimated by NMR and the presence of D-(-)-2-phenylbornylene (72) was confirmed by GLC*.

The divinylmercury (80) was isolated pure by crystallization (611 mg) as white needles (n-pentane), m.p. 136.5-138° (on standing in n-pentane it slowly converts to prisms m.p. 131-132° which crystallize on cooling with m.p. 136.5-138°), $[\alpha]_D^{25}$ -64° (c 1.04), ν_{max} 764, 701 cm^{-1}; λ_{max} 246 (ϵ 4140), 255 (ϵ 4160), 280 nm (ϵ 3990): NMR δ 7.20 (C^2phenyl); 2.38 ($J_{4-H, 5-exo-H}$ 3.0 Hz; C^4H); 0.99 ($C^{10}H_3$); 0.84 (C^9H_3); 0.78 ppm (C^8H_3): RD (c 0.19), 1 mm cell; $[\Phi]_{285}$ 0°; $[\Phi]_{297}$ -5170° (trough); $[\Phi]_{325}$ -817°; $[\Phi]_{350}$ -455°; $[\Phi]_{400}$ -159°: M^+ (for ^{202}Hg) 624.271364 ($C_{32}H_{38}Hg$ requires 624.267962), (Found: C, 62.1; H, 6.3. $C_{32}H_{38}Hg$ requires: C, 61.7; H, 6.2%).

(b). In aq. MeOH. As for (a). with D-(-)-2-phenylbornylene (72; 1.29 g) except replacing THF by MeOH and extending the reaction time to 4 hr. The reaction gave a mixture (788 mg) consisting of D-(-)-2-phenylbornylene (72; 24 mg, 4%) and (-)-di-(D-2-phenylborn-2-en-3-yl)-mercury (80; 764 mg, 90%) as estimated by NMR and GLC*.

* GLC at 150° on a 5' 10% PEG 1500 on Chromosorb P HMDS 60/80# column.

LAH reduction of (-)-di-(D-2-phenylborn-2-en-3-yl)-mercury (80)

LAH (1.00 g) was added to a soln of the divinylmercury

(80; 500 mg) in THF (100 ml) and the mixture heated under reflux for 4 hr. Decomposition of excess LAH by addition of $Na_2SO_4.10H_2O$ followed by an aq. soln of sodium potassium tartrate and isolation by means of ether gave pure (GLC*, NMR) D-(-)-2-phenylbornylene (72; 319 mg; 94%).

* GLC at 150° on a 5' 10% PEG 1500 on Chromosorb P HMDS 60/80# column.

Li-$EtNH_2$ reduction of D-(+)-2,3-exo-epoxy-2-endo-phenylbornane (49)[69]

Li (250 mg) was added to $EtNH_2$ (15 ml) in a flask equipped wtih a dry ice-acetone condenser. The blue soln that resulted was stirred for 2 hr to dissolve the Li. The epoxide (49; 100 mg) in $EtNH_2$ (5 ml) was then added and the mixture stirred for 1 hr. Isolation by means of ether gave D-(-)-2-endo-cyclohex-1'-en-1'-yl-3-exo-hydroxybornane (97; 73 mg, 72%) as crystals (sublimation), m.p. 95-96°, $[\alpha]_D^{29}$ -29° (c 1.09), ν_{max} 3605 cm^{-1}, NMR δ 5.45 ($W_{h/2}$ 6 Hz; olefinic proton $C^{2'}H$); 3.81 ($J_{2\text{-exo-H},3\text{-endo-H}}$ 4.6 Hz; $C^{3\text{-exo-}}H$); 2.35 ($W_{h/2}$ 8 Hz; $C^{2\text{-exo-}}H$); 1.85 ($C^{3\text{-exo-}}OH$); 1.14 (C^8H_3); 0.83 ppm (C^9H_3 and $C^{10}H_3$): (Found: C, 82.0; H, 11.4. $C_{16}H_{26}O$ requires: C, 82.0; H, 11.2%).

Li-$EtNH_2$ reduction of D-(-)-3-exo-hydroxy-2-endo-phenylbornane (96)[69]

Li (300 mg) was added to $EtNH_2$ (25 ml) in a flask equipped with a dry ice-acetone condenser. The blue soln that resulted

was stirred for 2 hr to dissolve the Li. The alcohol (96; 300 mg) was then added and the mixture stirred for 1 hr. Isolation by means of ether gave D-(-)-2-endo-cyclohex-1'-en-1'-yl-3-exo-hydroxybornane (97; 295 mg, 97%) as crystals (sublimation), m.p. and m.m.p. 95-96°, identical (IR, NMR, TLC) with an authentic sample.

D-3-exo-Deuterocamphor (44)[14,50]

Na (500 mg) was added slowly in small pieces over 30 min to a soln of D-(+)-camphor (43; 20.0 g) in dioxane (50 ml) and D_2O (10 ml) and the mixture stirred at 20° for 11 days. Isolation by means of n-pentane afforded D-3-exo-deuterocamphor (44; 31% d_1; 18.8 g, 94%).

The percentage d_1 content for D-3-exo-deuterocamphor (44) and the subsequent deuterated compounds (47 and 67) was determined via the equation:

$$y = \frac{100.(\overline{M+1}.M_o - M.\overline{M+1}_o)}{M_o.(M+\overline{M+1}) - M.\overline{M+1}_o},$$

y = the percentage d_1 incorporation,

M, $\overline{M+1}$ = the height of the M and M + 1 peaks respectively in the mass spectra of the deuterated compound,

M_o, $M+1_o$ = the height of the M and M + 1 peaks respectively in the mass spectra of the nondeuterated compound.

D-3-exo-Deutero-2-exo-hydroxy-2-endo-phenylbornane (47)[29]

Bromobenzene (23.5 g) in ether (35 ml) was added to Mg (3.75 g) in ether (650 ml) over 30 min and left to stir for a further 2 hr. A soln of D-3-exo-deuterocamphor (44; 18.6 g) in ether (50 ml) was then added over 10 min. After stirring at 20° for 19 hr saturated aq. NH_4Cl was added. Isolation by means of ether gave a crude product (23.8 g). Biphenyl and unreacted D-3-exo-deuterocamphor (44) were removed by steam distillation in the presence of $NaHCO_3$. Isolation by means of ether gave D-3-exo-deutero-2-exo-hydroxy-2-endo-phenylbornane (47; 48% d_1; 9.48 g, 34%) which crystallized on standing. Recrystallization from n-pentane gave massive prisms.

$SOCl_2$-Pyridine dehydration of D-3-exo-deutero-2-exo-hydroxy-2-endo-phenylbornane (47)

$SOCl_2$ (1 ml) was added to a soln of the alcohol (47; 1.00 g) in pyridine (20 ml) at -20° and the mixture stirred at -20° for 30 min. Isolation by means of ether gave a mixture (10% d_1; 817 mg, 89%) shown (GLC*, NMR) to consist of D-(-)-2-phenylbornylene (72; 703 mg, 86%) and 7-syn-deutero-1-phenylcamphene (67; 48% d_1; 114 mg, 14%).

Adsorption of this material onto silica gel (100 g) and elution with n-pentane gave D-(-)-2-phenylbornylene (72; 99% pure by GLC and NMR; 3.5% d_1; 157 mg).

Further elution with n-pentane gave a mixture of 72 and 67 (644 mg).

* GLC at 150° on a 5' 10% PEG 1500 on Chromosorb P HMDS 60/80# column.

(+)-1-Phenylcamphene (66)

D-(-)-2-exo-Hydroxy-2-endo-phenylbornane (46; 5.16 g) was adsorbed onto silica gel (250 g) and allowed to stand. After 30 min elution with n-pentane gave a mixture of D-(-)-2-phenylbornylene (72; 211 mg, 4%) and (+)-1-phenylcamphene (66; 401 mg, 8%) as estimated by GLC* and NMR.

Continued elution gave (-)-1-phenylcamphene (66; 4.03 g, 85%) as a liquid, n_D^{20} 1.5412, $[\alpha]_D^{22}$ +28° (c 1.00), ν_{max} 886, 758, 697 cm^{-1}: NMR δ 7.27, 7.24 (C^1phenyl); 4.56 (anti-2-methylene H); 4.18 (syn-2-methylene H)[112]; 1.14 (C^{3}-exo-Me and C^{3}-endo-Me): (Found: C, 90.9; H, 9.3. $C_{16}H_{20}$ requires: C, 90.5; H, 9.5%), contaminated with 7% of 72.

(lit.[94]: 1-phenylcamphene b.p.$_{16\ mm}$ 147°, n_D^{20} 1.5447).

* GLC at 150° on a 5' 10% PEG 1500 on Chromosorb P HMDS 60/80# column.

D-(-)-2-Phenylborn-2-ene (72)[31,53]

(a). D-(-)-2-endo-Hydroxy-2-exo-phenylbornane (173 g) in benzene (1 l) was added to NaH (145 g) in benzene (500 ml) all at once and the mixture was refluxed with stirring to give the sodium alkoxide (82). After 3 days it was cooled and CS_2 (500 ml) was added, stirred at 20° for 24 hr and then refluxed for 24 hr to give the sodium xanthate (83). The mixture was

then cooled and EtCl (500 ml) added, stirred for 2 days at 20° and then refluxed for 24 hr. After cooling the excess NaH was decomposed by H_2O. Isolation by means of ether gave the crude S-ethyl xanthate (84). After removal of the solvent the S-ethyl xanthate (224 g) was pyrolysed by heating to 200° for 3 hr. The crude product (174 g) showed signals in the NMR consistent with D-(-)-2-phenylbornylene (72) and (+)-1-phenyl-camphene (66) in the ratio 19:1. Absorption of the crude product onto silica gel (2 Kg) and elution initially gave 72 (ca. 98% pure by GLC*) followed by intermediate fractions consisting of 72 and 66 which became increasingly richer in the latter compound on continued elution. The intermediate fractions were successively recolumned to increase the amount of 72 obtained (ca. 98% pure by GLC*). This was then distilled on a 24" "Nester Faust" teflon spinning band. The total yield of pure (> 99% pure by GLC* and NMR) D-(-)-2-phenylbornylene (72) was 75 g (47%), b.p.$_{4.6\ mm}$ 122°, n_D^{23} 1.5462, $[\alpha]_D^{26}$ -196° (c 1.04), ν_{max} 829, 756, 697 cm^{-1}; λ_{max} 201 (inflexion, ϵ 15800), 214 (inflexion, ϵ 9600), 222 (inflexion, ϵ 7100), 251 nm (ϵ 11900): NMR δ 7.32 (C^2phenyl); 6.03 ($J_{3\text{-}H,4\text{-}H}$ 3.3 Hz; C^3H); 2.40 ($J_{3\text{-}H,4\text{-}H}$ 3.3, $J_{4\text{-}H,5\text{-}exo\text{-}H}$ 3.3 Hz; C^4H); 1.11 ($C^{10}H_3$); 0.91 (C^8H_3); 0.84 ppm (C^9H_3): (Found: C, 90.2; H, 9.7. $C_{16}H_{20}$ requires: C, 90.5; H, 9.5%).

(lit.[31]: 2-phenylbornylene b.p.$_{3.5\ mm}$ 96-98°).

(b). $SOCl_2$ (36 ml) was added over 15 min to a soln of D-(-)-2-exo-Hydroxy-2-endo-phenylbornane (46; 104 g) in pyridine

(700 ml) at -20° over 15 min and the mixture then stirred at -20° for 30 min. Isolation by means of n-pentane gave a mixture (90.9 g) shown (GLC*, NMR) to consist of D-(-)-2-phenylbornylene (72; 77.3 g, 81%) and (+)-1-phenylcamphene (66; 13.6 g, 14%). Adsorption of this material onto silica gel (1 Kg) and elution initially gave 72 (ca. 95% pure by GLC*) followed by intermediate fractions consisting of 72 and 66 which became increasingly richer in the latter compound on continued elution. The intermediate fractions were successively recolumned to increase the amount of 72 obtained (ca. 95% pure by GLC*). This was then distilled on a 24" "Nester Faust" teflon spinning band. The total yield of pure (> 99% pure by GLC*, NMR) D-(-)-2-phenylbornylene (72) was 62.2 g (65%), b.p.$_{4.6\ mm}$ 122°, identical (GLC*, NMR) with the previous sample.

* GLC at 150° on a 5' 10% PEG 1500 on Chromosorb P HMDS 60/80# column.

m-Chloroperbenzoic acid oxidation of D-(-)-2-phenylbornylene (72)[114,115]

(a). m-Chloroperbenzoic acid (10.0 g) was added to a soln of the olefin (72; > 99% pure by GLC*; 5.00 g) in $CHCl_3$ (100 ml) and the mixture stirred at 20° for 6 hr. Isolation by means of ether gave a terpenoid mixture (5.65 g) which was adsorbed onto activated alumina (300 g).

Elution with n-pentane gave D-(-)-2-phenylbornylene (72;

15 mg, 0.3%) as an oil, identical (IR, GLC*, NMR) to an authentic sample.

n-Pentane-benzene (19:1) gave 1-phenylcamphene exo-epoxide (85; 48 mg, 1%) as crystals (n-pentane), m.p. 93.5-95°, $[\alpha]_D^{29}$ 0° (c 1.04), ν_{max} 758, 698 cm^{-1}; λ_{max} 248 (ϵ 269), 253 (ϵ 294), 259 (ϵ 314), 265 (ϵ 242), 267 (inflexion, ϵ 186), 282 (shoulder, ϵ 67), 292 nm (shoulder, ϵ 49): NMR δ 7.24 (C^1phenyl); 2.49, 1.95 ($J_{2\text{-}CHH\text{-},2\text{-}CHH\text{-}}$ 4.8 Hz; C^2 epoxide methylene); 1.04 ($C^{3\text{-exo-}}$Me); 0.90 ppm ($C^{3\text{-endo-}}$Me): (Found: C, 84.4; H, 9.0. $C_{16}H_{20}O$ requires: C, 84.2; H, 8.8%).

Elution with n-pentane-benzene (3:1) and (1:1) gave D-(-)-2-endo-phenylbornan-3-one (87; 2.21 g, 41%) as needles (n-pentane), m.p. 95-96°, $[\alpha]_D^{26}$ -139° (c 1.06), ν_{max} 1746, 748, 697 cm^{-1}; λ_{max} 243 (shoulder, ϵ 85), 249 (ϵ 120), 253 (ϵ 170), 259 (ϵ 219), 265 (ϵ 177), 292 (shoulder, ϵ 47), 301 (ϵ 53), 311 (ϵ 49), 322 nm (shoulder, ϵ 26): NMR δ 7.37, 7.34, 7.29, 7.25, 7.08, 7.02, 6.95, 6.92 ($C^{2\text{-endo-}}$phenyl); 3.49 ($W_{h/2}$ 3 Hz; $C^{2\text{-exo-}}$H); 2.36 ($J_{4\text{-}H,5\text{-exo-}H}$ 4.4 Hz; C^4H); 1.09, 1.05, 0.99 ppm (C^8H_3, C^9H_3 and $C^{10}H_3$): RD (c 0.10); $[\Phi]_{256}$ -1320° (inflexion); $[\Phi]_{263}$ -1150° (trough); $[\Phi]_{270}$ -900° (trough); $[\Phi]_{283}$ 0°; $[\Phi]_{295}$ -357° (peak); $[\Phi]_{304}$ -52° (inflexion); $[\Phi]_{306}$ 0°; $[\Phi]_{314}$ -1100°(trough); $[\Phi]_{326}$ -2090° (trough); $[\Phi]_{350}$ -710°; $[\Phi]_{400}$ -311°; $[\Phi]_{450}$ -176°; $[\Phi]_{500}$ -102°; $[\Phi]_{599}$ -32°: (Found: C, 84.2; H, 9.1. $C_{16}H_{20}O$ requires: C, 84.2; H, 8.8%).

Benzene and benzene-ether (19:1) eluted (-)-7-syn-hydroxy-1-phenylcamphene exo-epoxide (86; 107 mg, 2%) as waxy crystals

(sublimation), m.p. 70° to a liquid-crystal phase, 100-105° cleared; $[\alpha]_D^{29}$ -79° (c 1.05), ν_{max} 3604, 759, 700 cm^{-1}; λ_{max} 232 (shoulder, ϵ 772), 245 (inflexion, ϵ 601), 259 (ϵ 435), 265 (ϵ 333), 279 (inflexion, ϵ 88) 290 nm (shoulder, ϵ 46): NMR δ 7.32 ($W_{h/2}$ 12 Hz; C^1phenyl); 4.51 ($J_{7\text{-anti-H},4\text{-H}}$ 1.6 Hz; $C^{7\text{-anti-H}}$); 2.70, 2.27 ($J_{2\text{-CHH-},2\text{-CHH-}}$ 4.6 Hz; C^2 epoxide methylene); 1.27 ($C^{3\text{-exo-Me}}$); 1.01 ppm ($C^{3\text{-endo-Me}}$): (Found: C, 78.9; H, 8.3. $C_{16}H_{20}O_2$ requires: C, 78.7; H, 8.3%).

Elution with benzene-ether (39:1) and (19:1) gave (+)-3-exo-hydroxy-2-phenyltricyclene (89; 288 mg) as needles (n-pentane), m.p. 85-88°, $[\alpha]_D^{29}$ +18° (c 1.05), ν_{max} 3614, 701 cm^{-1}; λ_{max} 255 (ϵ 249), 261 (ϵ 276), 266 (shoulder, ϵ 247), 276 (inflexion, ϵ 109), 291 nm (shoulder, ϵ 10): NMR δ 7.27 (C^2 phenyl); 4.48 ($J_{3\text{-endo-H},4\text{-H}}$ 1.8 Hz; C^3H); 1.49 ($C^{3\text{-exo-OH}}$); 1.03 (C^8H_3); 0.92 (C^9H_3); 0.83 ppm ($C^{10}H_3$): M^+ 228.151403 ($C_{16}H_{20}O$ requires 228.150506).

Continued elution with benzene-ether (19:1) and benzene-ether (9:1) gave a mixture of (+)-3-exo-hydroxy-2-phenyl-tricyclene (89; 444 mg) and an unknown (362 mg) as determined by NMR.

Benzene-ether (9:1) and (3:1) gave an unknown (297 mg) as needles (n-pentane), m.p. 104-106°, $[\alpha]_D^{29}$ +7° (c 1.00), ν_{max} 3638, 759, 699 cm^{-1}; λ_{max} 248 (shoulder, ϵ 179), 254 (ϵ 198), 260 (ϵ 220), 266 (ϵ 164), 269 nm (inflexion, ϵ 123): NMR δ 7.30 (phenyl); 3.71 (J 7.6, J' 6.2 Hz; H); 1.66 (OH); 1.20 (Me); 1.07 (Me); 0.90 ppm (Me): M^+ 232.146303 ($C_{15}H_{20}O_2$ requires

232.146006).

The total yield of 89 and unknown was 732 mg (14%) and 659 mg (12%).

(b). As for (a). except replacing $CHCl_3$ by CCl_4 and extending the reaction time to 20 hr.

Column chromatography as for (a). gave 1-phenylcamphene exo-epoxide (85; 57 mg, 1%), D-(-)-2-endo-phenylbornan-3-one (87; 2.53 g, 47%), (-)-7-syn-hydroxy-1-phenylcamphene exo-epoxide (88; 103 mg, 2%), (+)-3-exo-hydroxy-2-phenyltricyclene (89; 348 mg, 6%) and an unknown (534 mg, 10%).

(c). D-(+)-2-exo-Phenylbornan-3-one (88; 30 mg) was reacted under the same conditions as for (a). and (b). in an NMR tube. Analysis by NMR after reaction showed no epimerisation to the C^2 epimer (87).

* GLC at 150° on a 5' 10% PEG 1500 on Chromosorb P HMDS 60/80# column.

NBS - aq. DMSO reaction on D-(-)-2-phenylbornylene (72)[64]

NBS (1.95 g) was added to a stirred soln of D-(-)-2-phenylbornylene (72; 1.00 g) in DMSO (25 ml) and H_2O (313 mg) under an atmosphere of N_2 with cooling (< 20°). After 1 hr the reaction was quenched with H_2O and isolation by means of ether gave a semi-crystalline mixture (1.48 g). The product was treated as follows.

(a). Crystallization from n-pentane gave (+)-7-anti-bromo-1-phenylcamphene (70; 983 mg, 72%) as crystals (n-pentane

or sublimation), m.p. 82-83°, $[\alpha]_D^{25}$ +116° (c 0.97), ν_{max} 893, 743, 695 cm^{-1}; λ_{max} 243 (inflexion, ϵ 678), 248 (shoulder, ϵ 752), 252 (ϵ 809), 258 (ϵ 812), 264 nm (ϵ 667): NMR δ 7.31, 7.28 (C^1phenyl); 4.72 ($W_{h/2}$ 4 Hz; $C^{7\text{-}\underline{syn}\text{-}}H$); 4.70 (anti-2-methylene H); 4.22 (syn-2-methylene H)[112]; 1.24 ($C^{3\text{-}\underline{exo}\text{-}}Me$); 1.20 ppm ($C^{3\text{-}\underline{endo}\text{-}}Me$): (Found: C, 66.1; H, 6.8; Br, 27.8. $C_{16}H_{19}Br$ requires: C, 66.0; H, 6.6; Br, 27.4%).

(b). Analysis by GLC* showed five compounds with integral percentages 0.3, 6, 78, 8, 8 in order of decreasing R_f values.

The first compound had an R_f value identical with D-(-)-2-phenylbornylene (72).

Preparative GLC† gave the major compound (+)-7-anti-bromo-1-phenylcamphene (70; 45 mg) as crystals, m.p. and m.m.p. 82-83°, identical (IR, GLC , NMR) with the product obtained via (a).

The last product eluted was identical (GLC ,NMR of the crude product mixture) with D-(-)-3,10-dibromo-2-phenylbornylene (91) prepared via NBS - aq. DMSO on (+)-7-anti-bromo-1-phenyl-camphene (70).

* GLC at 100° on a 5' 5% SE-30 on Chromosorb P HMDS 60/80# column.

† GLC at 150° on a 5' 10% SE-30 on Chromosorb P HMDS 60/80# column.

D-(-)-3,10-Dibromo-2-phenylbornylene (91)[64]

NBS (390 mg) was added to a stirred soln of (+)-7-anti-bromo-1-phenylcamphene (70; 200 mg) in DMSO (5 ml) and H_2O (63 mg) under an atmosphere of N_2 with cooling (< 20°). After 8 hr the reaction was quenched with H_2O and isolation by means of ether gave almost pure D-(-)-3,10-dibromo-2-phenylbornylene (91; 242 mg, 95%) as a gum.

Analysis by GLC* showed one main compound and a trace of starting material. Purification by preparative GLC† gave D-(-)-3,10-dibromo-2-phenylbornylene (91; 20 mg) as a gum, $[\alpha]_D^{26}$ -10° (c 0.97), ν_{max} 763, 698 cm^{-1}; λ_{max} 247 nm (ϵ 6500), NMR δ 7.31 ($W_{h/2}$ 6 Hz; C^2phenyl); 3.58 (C^9CH_2Br); 2.56 ($J_{4-H, 5-exo-H}$ 2.7 Hz; C^4H); 1.18 (C^8H_3); 1.03 ppm (C^9H_3): (Found: C, 52.7; H, 5.1; Br, 41.8. $C_{16}H_{18}Br_2$ requires: C,51.9; H, 4.9; Br, 43.2%).

* GLC at 100° on a 5' 5% SE-30 on Chromosorb P HMDS 60/80 column.

† GLC at 150° on a 5' 10% SE-30 on Chromosorb P HMDS 60/80 column.

Hydroboration and alkaline hydrogen peroxide oxidation on D-(-)-2-phenylbornylene (72)[66,114,117]

(a). A soln (1 M) of $NaBH_4$ in diglyme (90 ml) was added over 1 hr to a stirred soln of BF_3-etherate in diglyme (20 ml) while a stream of dry N_2 was passed through the generator. The generator was then heated to 70-80° for 1 hr to ensure

complete transfer of diborane to the hydroboration flask. The diborane formed was passed through a stirred soln of D-(-)-2-phenylbornylene (72; 5.00 g) in THF (100 ml) at 20° for a further 26 hr and the excess diborane then decomposed by addition of H_2O (20 ml). The resulting organoboranes were oxidised by addition of a soln (3 M) of aq. NaOH (32 ml) and hydrogen peroxide (30%; 32 ml) with stirring at 20° for 1 hr. Isolation by means of n-pentane gave a mixture (5.42 g) which was adsorbed onto activated alumina (250 g).

Elution with n-pentane gave D-(-)-2-phenylbornylene (72; 44 mg, 1%) as estimated by GLC* and NMR.

Elution with n-pentane-benzene (1:1) gave D-(-)-2-*exo*-hydroxy-2-*endo*-phenylbornane (46; 169 mg, 3%) as crystals m.p. and m.m.p. 41-42°, identical (IR, NMR, TLC) with an authentic sample.

Benzene eluted D-(-)-3-*exo*-hydroxy-2-*endo*-phenylbornane (96; 1.45 g) as crystals (sublimation), m.p. 135-136°, $[\alpha]_D^{29}$ -62° (*c* 1.05), ν_{max} 3589, 751, 730, 701 cm^{-1}; λ_{max} 239 (inflexion, ϵ 54), 244 (shoulder, ϵ 87), 249 (ϵ 132), 254 (ϵ 184), 260 (ϵ 218), 262 (inflexion, ϵ 194), 266 (ϵ 164), 269 nm (ϵ 128): NMR δ 7.26 ($W_{h/2}$ 7 Hz; $C^{2\text{-}\underline{endo}}$-phenyl); 4.15 ($J_{2\text{-}\underline{exo}\text{-H},3\text{-}\underline{endo}\text{-H}}$ 4.4 Hz; $C^{3\text{-}\underline{endo}}$-H); 3.09 ($J_{2\text{-}\underline{exo}\text{-H},3\text{-}\underline{endo}\text{-H}}$ 4.4, $J_{2\text{-}\underline{exo}\text{-H},6\text{-}\underline{exo}\text{-H}}$ 1.7 Hz; $C^{2\text{-}\underline{exo}}$-H); 1.27 ($C^8H_3$); 0.93 ($C^9H_3$); 0.75 ppm ($C^{10}H_3$): (Found: C, 83.7; H, 9.8. $C_{16}H_{22}O$ requires: C, 83.4; H, 9.6%).

Further elution with benzene gave a mixture of D-(-)-3-

exo-hydroxy-2-endo-phenylbornane (96; 590 mg) and D-(+)-3-endo-hydroxy-2-exo-phenylbornane (98; 1.29 g) as estimated by NMR.

Continued elution with benzene and benzene-ether (1:1) gave D-(-)-3-endo-hydroxy-2-exo-phenylbornane (98; 1.33 g) as crystals (sublimation), m.p. 141.5-142.5°, $[\alpha]_D^{29}$ -4° (c 1.00), ν_{max} 3592, 746, 700 cm^{-1}; λ_{max} 240 (shoulder, ϵ 57), 245 (inflexion, ϵ 89), 250 (ϵ 135), 255 (ϵ 186), 261 (ϵ 225), 263 (inflexion, ϵ 192), 267 (ϵ 165), 270 nm (ϵ 123): NMR δ 7.27 ($C^{2\text{-exo-}}$phenyl); 4.92 ($J_{2\text{-endo-}H,3\text{-exo-}H}$ 6.5, $J_{3\text{-exo-}H,4\text{-}H}$ 3.7, $J_{3\text{-exo-}H,5\text{-exo-}H}$ 1.1 Hz; $C^{3\text{-exo-}}H$); 2.57 ($J_{2\text{-endo-}H,3\text{-exo-}H}$ 6.5 Hz; $C^{2\text{-endo-}}H$); 1.80 ($C^{3\text{-endo-}}OH$); 0.90 ($C^{10}H_3$); 0.88 (C^9H_3); 0.70 ppm (C^8H_3): (Found: C, 83.4; H, 9.8. $C_{16}H_{22}O$ requires: C, 83.4; H, 9.6%).

The total yield of 96 and 98 was 2.04 g (38%) and 2.62 g (48%) respectively.

(b). As for (a). except THF replaced by diglyme and at the end of the total reaction time (28 hr) the mixture was heated under reflux at 160° for 1 hr. Decomposition, oxidation and workup via the procedure given for (a). gave a mixture (8.25 g; diglyme present).

Column chromatography as for (a). gave D-(-)-2-phenylbornylene (72; 10 mg, 0.2%), D-(-)-3-exo-hydroxy-2-endo-phenylbornane (96; 2.69 g, 50%) and D-(-)-3-endo-hydroxy-2-exo-phenylbornane (98; 1.52 g, 28%).

* GLC at 150° on a 5' 10% PEG 1500 on Chromosorb P HMDS 60/80 column.

CrO_3-Pyridine oxidation of D-(-)-3-exo-hydroxy-2-endo-phenylbornane (96)

A soln of the alcohol (96; 200 mg) in pyridine (4 ml) was added to CrO_3 (200 mg) in pyridine (4 ml) and stirred at 20° for 26 hr. Isolation by means of n-pentane gave D-(-)-2-endo-phenylbornan-3-one (87; 175 mg; 88%) as crystals (n-pentane), m.p. and m.m.p. 95-96°, identical (IR, NMR, TLC) with an authentic sample.

D-(-)-3-endo-Hydroxy-2-endo-phenylbornane (99)

LAH (350 mg) was added to a soln of D-(-)-2-endo-phenylbornan-3-one (87; 187 mg) in ether (30 ml) and the mixture heated under reflux for 90 min. Decomposition of excess LAH by addition of $Na_2SO_4.10H_2O$ followed by H_2O, filtration and removal of solvent gave D-(-)-3-endo-hydroxy-2-endo-phenylbornane (99; 147 mg, 78%) as needles (n-pentane), m.p. 92-93°, $[\alpha]_D^{25}$ -11° (c 1.06), ν_{max} 3609, 759, 709 cm^{-1}; λ_{max} 244 (shoulder, ϵ 144), 249 (ϵ 178), 253 (ϵ 227), 259 (ϵ 266), 264 nm (ϵ 205): NMR δ 7.32 ($C^{2\text{-endo-}}$phenyl); 4.56 ($J_{2\text{-exo-H},3\text{-exo-H}}$ 9.9, $J_{3\text{-exo-H},4\text{-H}}$ 4.1, $J_{3\text{-exo-H},5\text{-exo-H}}$ 1.9 Hz; $C^{2\text{-exo-}}H$); 1.51 ($C^{3\text{-endo-}}OH$); 1.05 (C^8H_3); 0.99 (C^9H_3); 0.65 ppm ($C^{10}H_3$): (Found: C, 83.4; H, 9.9. $C_{16}H_{22}O$ requires: C, 83.4; H, 9.6%).

CrO_3-Pyridine oxidation of D-(+)-3-endo-hydroxy-2-exo-phenylbornane (98)

A soln of the alcohol (98; 500 mg) in pyridine (10 ml) was

added to CrO_3 (500 mg) in pyridine (10 ml) and stirred at 20° for 24 hr. Isolation by means of n-pentane gave D-(+)-2-exo-phenylbornan-3-one (88; 421 mg, 85%) as crystals (sublimation), m.p. 88-89°, $[\alpha]_D^{29}$ +26° (c 1.07), ν_{max} 1743, 744, 701 cm^{-1}; λ_{max} 239 (ε 187), 244 (ε 192), 249 (ε 194), 254 (ε 213), 260 (ε 241), 267 (ε 192), 270 (inflexion, ε 117), 280-296 (ε 41) to 328 nm (ε 9): NMR δ 7.23 ($W_{h/2}$ 3 Hz; C^{2}-exo-phenyl); 3.37 ($W_{h/2}$ 2 Hz; C^{2}-endo-H); 0.99, 0.96, 0.95 ppm ($C^{8}H_3$, $C^{9}H_3$ and $C^{10}H_3$): RD (c 0.12); $[\Phi]_{257}$ +1250° (peak); $[\Phi]_{265}$ +1350° (peak); $[\Phi]_{272}$ +1400° (peak); $[\Phi]_{304}$ 0°; $[\Phi]_{323}$ -1020° (trough); $[\Phi]_{350}$ -252°; $[\Phi]_{400}$ -37°; $[\Phi]_{440}$ 0°; $[\Phi]_{450}$ +16°; $[\Phi]_{500}$ +29°; $[\Phi]_{589}$ +26°: (Found: C, 84.2; H, 8.7. $C_{16}H_{20}O$ requires: C, 84.2; H, 8.8%).

Epimerisation of D-(+)-2-exo-phenylbornan-3-one (88)

(a). D-(+)-2-exo-Phenylbornan-3-one (88; 40 mg) was adsorbed onto activated alumina (10 g) and allowed to stand. After 2 hr elution with ether gave D-(-)-2-endo-phenylbornan-3-one (87; 39 mg, 98%) as needles (n-pentane), m.p. and m.m.p. 95-96°, identical (IR, NMR, TLC) with an authentic sample.

(b). As for (a). except activated alumina was replaced by 10% deactivated alumina. Elution after 2 hr gave 87 (39 mg, 98%).

(c). A soln (3 M) of aq. NaOH (2 ml) was added to a stirred soln of D-(+)-2-exo-phenylbornan-3-one (88; 31 mg) in THF (6 ml) and kept at 20° for 24 hr. Isolation by means of

ether gave 87 (29 mg, 94%).

D-(-)-3-exo-Hydroxy-2-exo-phenylbornane (100)

LAH (350 mg) was added to a soln of D-(+)-2-exo-phenylbornan-3-one (88; 200 mg) in ether (30 ml) and the mixture heated under reflux for 90 min. Decomposition of excess LAH by addition of $Na_2SO_4.10H_2O$ followed by H_2O, filtration and removal of solvent gave D-(-)-3-exo-hydroxy-2-exo-phenylbornane (100; 182 mg, 90%) as an oil, n_D^{22} 1.5471, $[\alpha]_D^{29}$ -127° (c 1.10), ν_{max} 3579, 723, 703 cm^{-1}; λ_{max} 238 (shoulder, ϵ 144), 244 (shoulder, ϵ 126), 250 (shoulder, ϵ 165), 254 (ϵ 206), 260 (ϵ 240), 262 (shoulder, ϵ 200), 265 (ϵ 190), 269 nm (ϵ 134): NMR δ 7.26 ($C^{2\text{-exo-}}$phenyl); 4.12 ($J_{2\text{-endo-H},3\text{-endo-H}}$ 7.9 Hz; $C^{3\text{-endo-}}H$); 3.23 ($J_{2\text{-endo-H},3\text{-endo-H}}$ 7.9 Hz; $C^{2\text{-endo-}}H$); ($C^{3\text{-exo-}}OH$); 1.35 ($C^{8}H_3$); 0.99 ($C^{10}H_3$); 0.93 ppm ($C^{9}H_3$): (Found: C, 83.2; H, 10.0. $C_{16}H_{22}O$ requires: C, 83.4; H, 9.6%).

$KMnO_4$ oxidation of D-(-)-2-phenylbornylene (72)

(a). A soln of $KMnO_4$ (18 g) and aq. NaOH (0.156 M) (800 ml) at 5-10° was quickly added to a stirred soln of D-(-)-2-phenylbornylene (72; 21.2 g) in t.-BuOH (1 l) and H_2O (700 ml) at 5-10°. The temperature was maintained between 5-10° in a cold room for 210 min and then sufficient sodium metabisulphite was added to remove any remaining potassium permanganate. The soln was filtered through "Celite Filteraid 545" and the residue washed with t.-BuOH (500 ml). The t.-BuOH was

distilled off under vacuum on a water bath, the aq. soln was saturated with NaCl and isolation by means of ether gave a neutral fraction (18.9 g). The aqueous soln was then acidified by the addition of dil. hydrochloric acid and isolation by means of ether gave an acid fraction (1.80 g).

The neutral fraction (19.9 g) was adsorbed onto activated alumina (1 Kg).

Elution with n-pentane gave D-(-)-2-phenylbornylene (72; 5.18 g, 24%) identical (GLC ,NMR) to an authentic sample.

n-Pentane-benzene (3:1) eluted (+)-7-keto-1-phenylcamphene (71; 1.01 g, 5%) as needles (n-pentane), m.p. 80-81°, $[\alpha]_D^{25}$ +42° (c 1.07), ν_{max} 1779, 880, 728, 698 cm^{-1}; λ_{max} 247 (ϵ 239), 252 (ϵ 268), 258 (ϵ 295), 265 (ϵ 223), 302 nm ($W_{h/2}$ 44 nm, ϵ 128): NMR δ 7.30, 7.27 ($W_{h/2}$ 4 Hz; C^1phenyl); 4.85 (anti-2-methylene H); 4.36 (syn-2-methylene H)[112]; 1.34 (C^3-endo-Me); 1.19 ppm (C^3-exo-Me): RD (c 0.11); $[\Phi]_{265}$ -4280° (trough); $[\Phi]_{273}$ -4380° (trough); $[\Phi]_{278}$ -4350° (trough); $[\Phi]_{303}$ 0°; $[\Phi]_{319}$ +3930 (peak); $[\Phi]_{350}$ +967°; $[\Phi]_{400}$ +357°; $[\Phi]_{450}$ +194°; $[\Phi]_{500}$ +124°; $[\Phi]_{589}$ +42°: (Found: C, 84.7; H, 8.4. $C_{16}H_{18}O$ requires: C, 84.9; H, 8.0%).

Elution with benzene gave D-(-)-2-endo-Phenylbornan-3-one (87; 74 mg, 0.3%) as needles (n-pentane), m.p. and m.m.p. 95-96°, identical (IR, NMR, TLC) with an authentic sample.

Further elution with benzene gave (-)-7-syn-hydroxy-1-phenylcamphene (68; 385 mg, 2%) as needles (n-pentane), m.p. 66-68°, $[\alpha]_D^{22}$ -43° (c 1.11), ν_{max} 3578, 880, 762, 703 cm^{-1};

λ_{max} 246 (inflexion, ϵ 346), 252 (ϵ 286), 259 (ϵ 266), 265 nm (ϵ 224): NMR δ 7.40 ($W_{h/2}$ 13 Hz; C^1phenyl); 4.88 (anti-2-methylene H); 4.54 (syn-2-methylene H)[112]; 4.17 ($J_{7\text{-anti-H},7\text{-syn-OH}}$ 4.7, $J_{7\text{-anti-H},4\text{-H}}$ 1.4 Hz[61]); 1.77 ($J_{7\text{-anti-H},7\text{-syn-OH}}$ 4.7 Hz; $C^{7\text{-syn-}}$OH); 1.42 ($C^{3\text{-exo-}}$Me); 1.21 ppm ($C^{3\text{-endo-}}$Me): (Found: C, 84.4; H, 9.1. $C_{16}H_{20}O$ requires: C, 84.2; H, 8.8%).

Benzene-ether (37:3) eluted D-(-)-2-exo-hydroxy-2-endo-phenylbornan-3-one (58; 592 mg, 2%) as a waxy solid (sublimation), m.p. 72-74°, $[\alpha]_D^{24}$ -88° (c 1.00), ν_{max} 3550, 1750, 762, 704 cm^{-1}; λ_{max} 252 (ϵ 279), 259 (ϵ 285), 265 (ϵ 239), 268 (shoulder, ϵ 137), 282 (ϵ 108), 303 (broad, ϵ 40): NMR δ 7.30 ($C^{2\text{-endo-}}$phenyl); 2.78 ($W_{h/2}$ 3 Hz; $C^{2\text{-exo-}}$OH); 2.37 ($J_{4\text{-H},5\text{-exo-H}}$ 4.2 Hz; C^4H); 1.24 (C^8H_3); 1.15 ($C^{10}H_3$); 1.02 ppm (C^9H_3): RD (c 0.10); $[\Phi]_{262}$ -603° (shoulder); $[\Phi]_{269}$ -400° (trough); $[\Phi]_{275}$ 0°; $[\Phi]_{293}$ +527° (peak); $[\Phi]_{305}$ 0°; $[\Phi]_{331}$ -1900° (trough); $[\Phi]_{350}$ -936°; $[\Phi]_{400}$ -386°; $[\Phi]_{450}$ -224°; $[\Phi]_{500}$ -138°; $[\Phi]_{589}$ -88°: (Found: C, 78.8; H, 8.4. $C_{16}H_{22}O_2$ requires: C, 78.7; H, 8.3%).

Elution with benzene-ether (3:1) gave D-(+)-2-endo-hydroxy-2-exo-phenylbornan-3-one (57; 2.03 g, 8%) as crystals (sublimation), m.p. 110-111°, $[\alpha]_D^{26}$ +61° (c 1.07), ν_{max} 3550, 3460, 1748, 760, 707 cm^{-1}; λ_{max} 253 (ϵ 252), 259 (ϵ 279), 264 (ϵ 236), 270 (ϵ 147), 282 (ϵ 51) to 299 (ϵ 43) to 340 nm (ϵ 16): NMR δ 7.31 ($C^{2\text{-exo-}}$phenyl); 2.62 ($W_{h/2}$ 9 Hz; $C^{2\text{-endo-}}$OH); 2.40 ($J_{4\text{-H},5\text{-exo-H}}$ 4.0 Hz; C^4H); 1.14 ($C^{10}H_3$); 0.98

(C^9H_3); 0.82 ppm (C^8H_3): RD (c 0.12); $[\Phi]_{264}$ +2600° (shoulder); $[\Phi]_{272}$ +2470° (peak); $[\Phi]_{293}$ +2230° (peak); $[\Phi]_{325}$ 0°; $[\Phi]_{337}$ -972° (trough); $[\Phi]_{350}$ -436°; $[\Phi]_{379}$ 0°; $[\Phi]_{400}$ +61°; $[\Phi]_{450}$ +83°; $[\Phi]_{500}$ +83°; $[\Phi]_{589}$ +61°: (Found: C, 78.3; H, 8.6. $C_{16}H_{20}O_2$ requires: C, 78.7; H, 8.3%).

Benzene-ether (1:1) eluted D-(-)-2-exo,3-exo-dihydroxy-2-endo-phenylbornane (59; 5.76 g, 23%) as needles (n-pentane), m.p. 114-115°, $[\alpha]_D^{26}$ -32° (c 1.02), ν_{max} 3595, 3510, 769, 756, 725, 704 cm^{-1}; λ_{max} 243 (shoulder, ϵ 91), 248 (ϵ 124), 252 (ϵ 170), 259 (ϵ 212), 265 (ϵ 162), 269 (ϵ 92): NMR δ 7.37 ($W_{h/2}$ 12 Hz; $C^{2\text{-endo-}}$phenyl); 4.29 ($C^{3\text{-endo-}}$H); 2.87 ($W_{h/2}$ 10 Hz; $C^{2\text{-exo-}}$OH and $C^{3\text{-exo-}}$OH); 1.85 ($J_{4\text{-H},5\text{-exo-H}}$ 3.9 Hz; C^4H); 1.31 (C^8H_3); 0.92 ($C^{10}H_3$); 0.87 ppm (C^9H_3): (Found: C, 78.3; H, 9.0. $C_{16}H_{22}O_2$ requires: C, 78.0; H, 9.0%).

(b). As for (a). except the neutral fraction (18.9 g) was adsorbed onto 10% deactivated alumina (1 Kg).

Elution with n-pentane and n-pentane-benzene (3:1) gave fractions containing mixtures of D-(-)-2-phenylbornylene (72), (+)-7-keto-1-phenylbornylene (71), D-(-)-2-endo-phenylbornan-3-one (87), (-)-7-syn-hydroxy-1-phenylcamphene (68), D-(-)-2-exo-hydroxy-2-endo-phenylbornan-3-one (58) and D-(+)-2-endo-hydroxy-2-exo-phenylbornan-3-one (57).

n-Pentane-benzene (1:1) and benzene eluted D-(-)-2-exo,3-exo-dihydroxy-2-endo-phenylbornane (59; 4.84 g) as needles (n-pentane), m.p. and m.m.p. 114-115°, identical (IR, NMR, TLC) with an authentic sample.

Elution with benzene-ether (9:1) gave a mixture of D-(-)-2-exo,3-exo-dihydroxy-2-endo-phenylbornane (59; 924 mg) and D-(-)-2-endo,3-endo-dihydroxy-2-exo-phenylbornane (92; 423 mg) as estimated by NMR and TLC.

Benzene-ether (3:1) eluted D-(-)-2-endo,3-endo-dihydroxy-2-exo-phenylbornane (92; 57 mg) as crystals (sublimation), m.p. 98-99°, $[\alpha]_D^{24}$ -34° (c 1.05), ν_{max} 3587, 3541, 753, 701 cm^{-1}; λ_{max} 246 (shoulder, ϵ 222), 249 (ϵ 223), 254 (ϵ 250), 260 (ϵ 275), 266 (ϵ 222), 270 nm (shoulder, ϵ 143): NMR δ 7.41 ($W_{h/2}$ 16 Hz; $C^{2\text{-exo-phenyl}}$); 4.89 ($J_{3\text{-exo-H},4\text{-H}}$ 4.0 Hz; $C^{3\text{-exo-H}}$); 2.49 ($W_{h/2}$ 12 Hz; $C^{2\text{-endo-OH}}$ and $C^{3\text{-endo-OH}}$); 0.90 (C^9H_3 and $C^{10}H_3$); 0.72 ppm (C^8H_3): (Found: C, 77.7; H, 9.1. $C_{16}H_{22}O_2$ requires: C, 78.0; H, 9.0%).

The total yield of 59 and 92 was 5.76 g (23%) and 480 mg (2%) respectively.

* GLC at 150° on a 5' 10% PEG 1500 on Chromosorb P HMDS 60/80# column.

LAH reduction of (-)-7-Keto-1-phenylcamphene (71)

LAH (1.20 g) was added to a soln of the ketone (71; 6.13 mg) in ether (100 ml) and the mixture heated under reflux for 90 min. Decomposition of excess LAH by addition of $Na_2SO_4 \cdot 10H_2O$ followed by H_2O, filtration and removal of solvent gave (-)-7-syn-hydroxy-1-phenylcamphene (68; 601 mg, 97%) as needles (n-pentane), m.p. and m.m.p. 80-81°, identical (IR, NMR, TLC) with an authentic sample.

Na-EtOH reduction of (+)-7-keto-1-phenylcamphene (71)[69]

Na (1.00 g) was added slowly to a soln of the ketone (71; 350 mg) in EtOH (12.5 ml) over 30 min while heated under reflux. After the Na had dissolved (1 hr), isolation by means of ether gave a mixture (294 mg) which was adsorbed onto activated alumina (30 g).

Elution with benzene gave (-)-7-syn-hydroxy-1-phenylcamphene (68; 48 mg; 14%) as needles (n-pentane), m.p. and m.m.p. 81-82°, identical (IR, NMR, TLC) with an authentic sample.

Benzene-ether (19:1) and ether gave (+)-7-anti-hydroxy-1-phenylcamphene (69; 192 mg, 54%) as fine needles (n-pentane), m.p. 107.5-109°, $[\alpha]_D^{29}$ +54° (c 1.05), ν_{max} 3599, 890, 765, 702 cm^{-1}; λ_{max} 243 (ϵ 149), 249 (ϵ 164), 254 (ϵ 196), 260 (ϵ 219), 266 (ϵ 154), 269 nm (inflexion, ϵ 100): NMR δ 7.30 (C^1phenyl); 4.64 (anti-2-methylene H); 4.54 ($W_{h/2}$ 4 Hz; $C^{7\text{-syn-}}$H); 4.18 (syn-2-methylene H[112]); 1.65 ($W_{h/2}$ 4.5 Hz; $C^{7\text{-anti-}}$OH); 1.15 ppm ($C^{3\text{-endo-}}$Me and $C^{3\text{-exo-}}$Me): (Found: C, 83.9; H, 9.0. $C_{16}H_{20}O$ requires: C, 84.2; H, 8.8%).

CrO_3-Pyridine oxidation of (-)-7-syn-hydroxy-1-phenylcamphene (68)

A soln of the alcohol (68; 42 mg) in pyridine (0.5 ml) was added to CrO_3 (50 mg) in pyridine (0.5 ml) and stirred at 20° for 16 hr. Isolation by means of n-pentane gave (+)-7-keto-1-phenylcamphene (71; 40 mg, 96%) as needles (n-pentane), m.p.

and m.m.p. 80-81°, identical (IR, NMR, TLC) with an authentic sample.

CrO_3-Pyridine oxidation of (+)-7-anti-hydroxy-1-phenylcamphene (69)

A soln of the alcohol (69; 44 mg) in pyridine (1 ml) was added to CrO_3 (150 mg) in pyridine (0.5 ml) and stirred at 20° for 60 hr. Isolation by means of n-pentane gave (+)-7-keto-1-phenylcamphene (71; 38 mg, 87%) as needles (n-pentane), m.p. and m.m.p. 80-81°, identical (IR, NMR, TLC) with an authentic sample.

LAH reduction[118] of D-(-)-2-exo-hydroxy-2-endo-phenylbornan-3-one (58)

LAH (450 mg) was added to a soln of the ketol (58; 355 mg) in ether (40 ml) and the mixture heated under reflux for 4 hr. Decomposition of excess LAH by addition of $Na_2SO_4.10H_2O$ followed by an aq. soln of sodium potassium tartrate and isolation of the terpenoid material via ether gave a mixture (334 mg) consisting of two compounds (TLC).

Adsorption of the material onto activated alumina (25 g) and elution with benzene-ether (3:1) and benzene-ether (1:1) gave fractions initially rich in D-(-)-2-exo,3-exo-dihydroxy-2-endo-phenylbornane (59) as needles (n-pentane), m.p. and m.m.p. 114-115°, identical (IR, NMR, TLC) with an authentic sample.

Further elution with benzene-ether (1:1) gave fractions increasingly enriched in another diol (94) until ether-MeOH (20:1) eluted pure (NMR, TLC) D-2-exo,3-endo-dihydroxy-2-endo-phenylbornane (94) as crystals (sublimation), m.p. 106-109°, $[\alpha]_D^{24}$ 0° (c 1.09), ν_{max} 3612, 757, 702 cm^{-1}; λ_{max} 252 (shoulder, ϵ 388), 259 (ϵ 340), 265 (ϵ 254), 268 nm (shoulder, ϵ 189): NMR δ 7.61 ($W_{h/2}$ 9 Hz) and 7.25 ($W_{h/2}$ 7 Hz) ($C^{2\text{-endo}}$-phenyl); 4.38 ($J_{3\text{-exo-H},4\text{-H}}$ 4.4, $J_{3\text{-exo-H},5\text{-exo-H}}$ 0.9 Hz; $C^{3\text{-exo}}$-H); 2.28 ($W_{h/2}$ 8 Hz; $C^{2\text{-endo}}$-OH and $C^{3\text{-exo}}$-OH); 1.23 (C^8H_3); 0.93 (C^9H_3); 0.74 ppm ($C^{10}H_3$): (Found: C, 77.7; H, 9.2. $C_{16}H_{22}O_2$ requires: C, 78.0; H, 9.0%).

The total yield of 59 and 94 as estimated by NMR was 44 mg (12%) and 204 mg (57%) respectively.

CrO_3-Pyridine oxidation of D-(-)-2-exo,3-exo-dihydroxy-2-endo-phenylbornane (59)

A soln of the diol (59; 1.93 g) in pyridine (20 ml) was added to CrO_3 (2 g) in pyridine (20 ml) and stirred at 20° for 40 hr. Isolation by means of n-pentane gave D-(-)-2-exo-hydroxy-2-endo-phenylbornan-3-one (58; 1.22 g; 63%) as a waxy solid (sublimation), m.p. and m.m.p. 72-74°, identical (IR, NMR, TLC) with an authentic sample.

LAH reduction of D-(+)-2-endo-hydroxy-2-exo-phenylbornan-3-one (57)

LAH (1.40 g) was added to a soln of the ketol (57; ca. 95%

pure by TLC; 654 mg) in ether (100 ml) and the mixture heated under reflux for 4 hr. Decomposition of excess LAH by addition of $Na_2SO_4.10H_2O$ followed by an aq. soln of sodium potassium tartrate and isolation of the terpenoid material *via* ether gave a mixture (662 mg) consisting mainly of two compounds (TLC). Crystallization with n-pentane-ether gave pure D-(-)-2-*endo*,3-*exo*-dihydroxy-2-*exo*-phenylbornane (61; 277 mg) as crystals (sublimation), m.p. 108-109°, $[\alpha]_D^{24}$ -87° (*c* 0.43), ν_{max} 3599, 771, 709 cm^{-1}; λ_{max} 246 (shoulder, ϵ 60), 251 (shoulder, ϵ 78), 255 (ϵ 102), 261 (ϵ 128), 268 (ϵ 101), 271 nm (shoulder, ϵ 57): NMR δ 7.51 ($W_{h/2}$ 10 Hz), 7.18 ($W_{h/2}$ 8 Hz) (C^{2}-*exo*-phenyl); 3.78 (C^{3}-*endo*-H); 1.72 ($W_{h/2}$ 5 Hz; C^{2}-*endo*-OH and C^{3}-*exo*-OH); 1.14 ($C^{10}H_3$); 1.10 ($C^{8}H_3$); 0.97 ($C^{9}H_3$): (Found: C, 77.8; H, 9.2. $C_{16}H_{22}O_2$ requires: C, 78.0; H, 9.0%).

Adsorption of the mother liquor (383 mg) onto 5% deactivated alumina (20 g) and elution with benzene-ether (9:1) gave D-(-)-2-*endo*,3-*exo*-dihydroxy-2-*exo*-phenylbornane (61; 137 mg) as crystals (n-pentane-ether), m.p. and m.m.p. 108-109°, identical (IR, NMR, TLC) with the previous sample.

Ether eluted D-(-)-2-*endo*,3-*endo*-dihydroxy-2-*exo*-phenylbornane (92; 101 mg) as crystals (sublimation), m.p. amd m.m.p. 98-99°, identical (IR, NMR, TLC) with an authentic sample.

The total yield of 61 and 92 as estimated by NMR was 414 mg (63%) and 101 mg (15%) respectively.

D-(+)-2,3-exo-Epoxy-2-endo-phenylbornane (49)

A soln (1 M) of t.-BuOK in t.-BuOH (1 ml) was added to a soln of D-(+)-2-exo-hydroxy-2-endo-phenyl-3-exo-p-tolyl-sulphonyloxybornane (60; 250 mg) in t.-BuOH (0.5 ml) and kept at 70° for 15 min. Isolation by means of ether gave D-(+)-2,3-exo-epoxy-2-endo-phenylbornane (49; 126 mg, 88%) as a gum, n_D^{18} 1.5440, $[\alpha]_D^{29}$ +57° (c 1.07), ν_{max} 917, 755, 745, 690 cm^{-1}; λ_{max} 252 (ϵ 310), 258 (ϵ 342), 264 (ϵ 287), 269 nm (inflexion, ϵ 148): NMR δ 7.38, 7.36 ($C^{2\text{-endo-}}$phenyl); 3.39 ($J_{3\text{-endo-H},4\text{-H}}$ 1.3 Hz; $C^{3\text{-endo-}}H$); 2.13 ($W_{h/2}$ 6 Hz; C^4H); 1.25 (C^8H_3); 1.02 ($C^{10}H_3$); 0.84 ppm (C^9H_3): (Found: C, 84.0; H, 9.1. $C_{16}H_{20}O$ requires: C, 84.2; H, 8.8%).

The compound is unstable and completely rearranges after standing 24 hr at 20°.

D-(+)-2-endo-Hydroxy-2-exo-phenyl-3-endo-p-tolylsulphonyloxybornane (93)

p-Tolylsulphonyl chloride (272 mg) was added to D-(-)-2-endo,3-endo-dihydroxy-2-exo-phenylbornane (92; 136 mg) in pyridine (1 ml) and kept at 20° for 35 days. Isolation by means of ether gave D-(+)-2-endo-hydroxy-2-exo-phenyl-3-endo-p-tolysulphonyloxybornane (93; 216 mg, 98%) as crystals n-pentane), m.p. 124-125.5°, $[\alpha]_D^{29}$ +12° (c 1.08), ν_{max} 3587, 3523, 1373, 1189, 1177, 815, 754, 704 cm^{-1}; λ_{max} 251 (inflexion, ϵ 464), 256 (shoulder, ϵ 574), 261 (ϵ 656), 266 (ϵ 601), 274 nm (ϵ 428): NMR doublet centred at δ7.81 ($J_{ortho\text{-H},meta\text{-H}}$ 8.4 Hz;

tolyl-ortho-H); 7.32 ($J_{ortho\text{-}H,meta\text{-}H}$ 8.4 Hz; tolyl-meta-H and C^{2}-exo-phenyl); 5.66 ($J_{3\text{-}exo\text{-}H,4\text{-}H}$ 4.6 Hz; C^{3}-exo-H); 2.43 (tolyl-Me); 0.88 ($C^{9}H_3$); 0.82 ($C^{10}H_3$); 0.77 ppm ($C^{8}H_3$): (Found: C, 69.3; H, 7.3; S, 8.2. $C_{23}H_{28}O_4S$ requires: C, 69.0; H, 7.1; S, 8.0%).

D-2,3-endo-Epoxy-2-exo-phenylbornane (50)

A soln (1 M) of t.-BuOK in t.-BuOH (1 ml) was added to a soln of D-(+)-2-endo-hydroxy-2-exo-phenyl-3-endo-p-tolylsulphonyloxybornane (93; 173 mg) in t.-BuOH (1 ml) and kept at 70° for 15 min. Isolation by means of ether gave a mixture (84 mg) shown (NMR) to consist of only D-(-)-2-endo-phenylbornan-3-one (87; 53 mg, 54%) and D-2,3-endo-epoxy-2-exo-phenylbornane (50; 31 mg, 31%).

Subtraction of the NMR spectrum of 87 from that of the mixture gave the NMR of D-2,3-endo-epoxy-2-exo-phenylbornane (50) δ 3.83 ($J_{3\text{-}exo\text{-}H,4\text{-}H}$ 3.3 Hz; C^{3}-exo-H); 1.27 ($C^{10}H_3$); 0.85, 0.83 ppm ($C^{8}H_3$ and $C^{9}H_3$). Similarly ν_{max} 755, 699 cm^{-1} (no OH absorption present).

D-2-exo,3-exo-Dihydroxy-2-endo-phenylbornane cyclic sulphites (95a and 95b)

$SOCl_2$ (3 ml) was added to a soln of D-(-)-2-exo,3-exo-dihydroxy-2-endo-phenylbornane (59; 3.00 g) in pyridine-ether (2:5; 210 ml) and the mixture stirred ar 0° for 1 hr. Isolation by means of ether gave D-2-exo,3-exo-dihydroxy-2-

endo-phenylbornane cyclic sulphite (95a and 95b; 3.56 g, 100%) consisting of a mixture of anti-D-(+)-2-exo,3-exo-dihydroxy-2-endo-phenylbornane cyclic sulphite (95a; 71%) and syn-D-2-exo, 3-exo-dihydroxy-2-endo-phenylbornane cyclic sulphite (95b; 29%) as estimated by NMR.

Crystallization (ether) gave pure (NMR) anti-D-(+)-2-exo, 3-exo-dihydroxy-2-endo-phenylbornane cyclic sulphite (95a; 1.75 g) as crystals, m.p. 114-115°, $[\alpha]_D^{29}$ +169° (c 1.00), ν_{max} 1216, 968, 945, 906, 791, 712, 700 cm^{-1}; λ_{max} 269 (shoulder, ϵ 87), 265 (ϵ 209), 259 (ϵ 261), 253 (ϵ 193), 249 (shoulder, ϵ 126), 244 nm (shoulder, ϵ 88): NMR δ 7.40 ($W_{h/2}$ 4 Hz; C^{2}-endo-phenyl); 5.35 (C^{3}-endo-H); 2.31 ($J_{4\text{-}H,5\text{-}exo\text{-}H}$ 4.7 Hz; $C^{4}H$); 1.14 ($C^{8}H_3$); 1.01 ($C^{10}H_3$); 0.93 ppm ($C^{9}H_3$): (Found: C, 65.9; H, 6.9; S, 11.3. $C_{16}H_{20}O_3S$ requires: C, 65.7; H, 6.9; S, 11.0%).

The mother liquor (1.80 g) consisted of 95a (43%) and 95b (57%) as estimated by NMR, (Found: C, 65.9; H, 6.9; S, 11.3. $C_{16}H_{20}O_3S$ requires: C, 65.7; H, 6.9; S, 11.0%).

Subtraction of the NMR spectrum of 95a from that of the mixture gave the NMR of syn-D-2-exo,3-exo-dihydroxy-2-endo-phenylbornane cyclic sulphite (95b) δ 7.42 ($W_{h/2}$ 3 Hz; C^{2}-endo-phenyl); 4.85 (C^{3}-endo-H); 2.32 ($J_{4\text{-}H,5\text{-}exo\text{-}H}$ 5.1 Hz; $C^{4}H$); 1.50 ($C^{8}H_3$); 1.00 ($C^{10}H_3$); 0.96 ppm ($C^{9}H_3$). Similarly ν_{max} 1229, 995, 952, 770, 711, 702 cm^{-1}.

cis- and trans-But-2-ene[74]

A mixture of butan-1-ol (666 g) and aq. H_2SO_4 (60%, 1.5 l)

was refluxed and the cis- and trans-but-2-ene (187 g, 37%) was passed successively through a soln (8 M) of aq. NaOH, aq. H_2SO_4 (50-55%), dried over $CaCl_2$ and condensed in a tared ampoule at -15 to -20°.

D,L-erythro-3-Chlorobutan-2-ol (111) and D,L-threo-3-Chlorobutan-2-ol (110)[74]

cis- and trans-But-2-ene (132 g) was added to a mixture of calcium hypochlorite (640 g; 30% available Cl_2) and NaOH (200 g) in ice-H_2O (800-1000 g) at -10° to -15°. HAc (380 ml) was then added over 2 hr with stirring. Isolation by means of ether and distillation gave a mixture of D,L-2,3-dichlorobutane (112) and meso-2,3-dichlorobutane (114) (11 g, 4%) b.p.$_{80\ mm}$ 50-60° followed by a mixture of D,L-erythro-3-chlorobutan-2-ol (111) and D,L-threo-3-chlorobutan-2-ol (110) (106 g, 42%) b.p.$_{30\ mm}$ 50-60°, n_D^{21} 1.4374, NMR (CCl_4) δ 3.95 ($W_{h/2}$ 25 Hz; C^2H and C^3H); 3.22 (C^2OH); major signals at 1.50, 1.40 and minor signals at 1.53, 1.43 ($J^{app.}_{3\text{-}H,3\text{-}Me}$ 6.2 Hz; C^3Me); 1.21 ppm ($J_{2\text{-}H,2\text{-}Me}$ 6.0 Hz; C^2Me).

(lit.[74] : D,L- and meso-2,3-dichlorobutane (112 and 114) b.p.$_{80\ mm}$ 50-60°, D,L-erythro- and D,L-threo-3-chlorobutan-2-ol (111 and 110) b.p.$_{30\ mm}$ 50-60°).

cis- and trans-2,3-Epoxybutanes (108 and 109)[74]

A mixture of D,L-erythro- and D,L-threo-3-chlorobutan-2-ol (111 and 110; 193 g) was added to a soln of KOH (450 g) in H_2O

(250 ml) over 2 hr at 90°with stirring. A slow stream of N_2 was passed through the system after complete reaction to carry over any residual low b.p. compounds. The product was dried over anhydrous K_2CO_3 and distilled to give pure 2,3-epoxybutane (> 99% by GLC) (67.0 g, 52%) consisting of a mixture of cis-2,3-epoxybutane (108; 30%) and trans-2,3-epoxybutane (109; 70%) as estimated by GLC*.

Distillation on an 18" "Nester Faust" teflon spinning band gave pure (> 99% by GLC*) trans-2,3-epoxybutane (109; 38.3 g) b.p.$_{748\ mm}$ 53-54°, n_D^{17} 1.3748, NMR (CCL_4) δ 2.44 ($W_{h/2}$ 7 Hz; C^2H and C^3H); 1.16 ppm($J_{2\text{-}H,2\text{-}Me}$ and $_{3\text{-}H,3\text{-}Me}$ 4.4 Hz; C^2Me and C^3Me).

Continued distillation gave mixed fractions (4.2 g) followed by pure (> 99% by GLC*) cis-2,3-epoxybutane (108; 18.0 g) b.p.$_{748\ mm}$ 60-61°, n_D^{17} 1.3834, NMR (CCl_4) δ 2.76 ($W_{h/2}$ 10 Hz; C^2H and C^3H); major signals at 1.19, 1.10 and minor signals at 1.17, 1.13 ppm($J^{app.}_{2\text{-}H,2\text{-}Me}$ and $_{3\text{-}H,3\text{-}Me}$ 4.1 Hz; C^2Me and C^3Me).

(lit.[74]: trans-2,3-epoxybutane (109) b.p.$_{747\ mm}$ 53.6-54.1°, n_D^{20} 1.3736; cis-2,3-epoxybutane (108) b.p.$_{747\ mm}$ 59.9-60.4°).

* GLC at 50° on a 3' 20% Carbowax 20M on Chromosorb P 45/60# column.

D,L- and meso-Butan-2,3-diol (113 and 115)

Technical butan-2,3-diol which consisted of D,L- and meso-butan-2,3-diol (113 and 115; 1:1) was distilled on an 18"

"Nester Faust" teflon spinning band to give pure (> 99% by GLC*) D,L-butan-2,3-diol (113) b.p.$_{16\ mm}$ 85-86°, n_D^{25} 1.4298, NMR (CCl_4) δ 4.26 ($J_{2\text{-}H,2\text{-}OH}$ and $_{3\text{-}H,3\text{-}OH}$ 2.7 Hz; C^2OH and C^3OH); 3.33 ($W_{h/2}$ 12.5 Hz; C^2H and C^3H); 1.07 ppm ($J_{2\text{-}H,2\text{-}Me}$ and $_{3\text{-}H,3\text{-}Me}$ 5.5 Hz; C^2Me and C^3Me).

Continued distillation gave mixed fractions followed by pure (> 99% by GLC*) meso-butan-2,3-diol (115) as crystals, m.p. 33.5-34.5°, b.p.$_{16\ mm}$ 88-89°, n_D^{25} 1.4347, NMR (CCl_4) δ 3.69 ($W_{h/2}$ 6.4 Hz; C^2H and C^3H); 3.39 (C^2OH and C^3OH); 1.07 ppm ($J_{2\text{-}H,2\text{-}Me}$ and $_{3\text{-}H,3\text{-}Me}$ 6.4 Hz; C^2Me and C^3Me).

(lit.[74]: D,L-butan-2,3-diol (113) b.p.$_{16\ mm}$ 86°; meso-butan-2,3-diol (115) m.p. 34.4°, b.p.$_{16\ mm}$ 89°).

* GLC at 100° on a 5' 5% FFAP on Chromosorb P 60/80# column.

D,L-amphi-Butan-2,3-diol cyclic sulphite (116) and meso-anti- and meso-syn-butan-2,3-diol cyclic sulphites (117a and 117b)

$SOCl_2$ (30 ml) in ether (50 ml) was added to a soln of the diol (113 or 115; 15.0 g) in ether (100 ml) and pyridine (50 ml) over 2 hr with stirring. It was stirred a further 24 hr and then H_2O added over 1 hr. Isolation by means of ether and distillation gave the cyclic sulphite(s) (116 or 117a and 117b).

D,L-Butan-2,3-diol (113) gave pure (> 99% by GLC*) (116; 15.6 g, 69%) b.p.$_{18\ mm}$ 71-72°, n_D^{20} 1.4230, ν_{max} (smear) 1211 cm^{-1}, NMR (CCl_4) δ 4.50 ($J_{anti\text{-}H,syn\text{-}H}$ 8.5, $J_{anti\text{-}Me,syn\text{-}H}$ 6.0

Hz; syn-H); 3.98 ($J_{syn\text{-}H,anti\text{-}H}$ 8.5, $J_{syn\text{-}Me,anti\text{-}H}$ 6.0 Hz; anti-H[73]); 1.47 ($J_{anti\text{-}H,syn\text{-}Me}$ 6.0 Hz; syn-Me); 1.39 ppm ($J_{syn\text{-}H,anti\text{-}Me}$ 6.0 Hz; anti-Me[73]).

meso-Butan-2,3-diol gave pure (> 99% by GLC*) meso-butan-2,3-diol cyclic sulphites (117; 9.96 g, 44%) consisting of a mixture of meso-anti- and meso-syn-cyclic sulphites (117a and 117b) in the ratio 7:2 as estimated by GLC* and NMR, b.p.$_{18\ mm}$ 81-82°, n_D^{20} 1.4370, ν_{max} (smear) 1207 cm^{-1}, NMR (CCl_4) (117a) δ 4.92 ($W_{h/2}$ 9 Hz; C^2H and C^3H); major signals at 1.32, 1.22 and minor signals at 1,29, 1.24 ($J^{app.}_{2\text{-}H,2\text{-}Me}$ and $_{3\text{-}H,3\text{-}Me}$ 4.7 Hz; C^2Me and C^3Me); (117b) 4.53 ($W_{h/2}$ 10 Hz; C^2H and C^3H); major signals at 1.55, 1.44 and minor signals at 1.52, 1.47 ppm ($J^{app.}_{2\text{-}H,2\text{-}Me}$ and $_{3\text{-}H,3\text{-}Me}$ 4.7 Hz; C^2Me and C^3Me); integral ratio of 117a and 117b was 7:2.

A partial separation of 117a which has a slightly greater R_f value than 117b was obtained by preparative GLC† to give a mixture (21 mg) consisting of 117a and 117b in the ratio 13:1 as estimated by GLC* and NMR.

(lit.[77]: D-(-)-amphi-butan-2,3-diol cyclic sulphite b.p.$_{10\ mm}$ 60.5-60.7°, b.p. 177-178°; n_D^{25} 1.4296 and 1.4300: meso-butan-2,3-diol cyclic sulphite (117) b.p.$_{8\ mm}$ 67°, b.p.$_{14\ mm}$ 74-76°, b.p.$_{17\ mm}$ 70-71°, b.p. 188-189°; n_D^{25} 1.4368 and 1.4380).

* GLC at 100° on a 3' 20% Carbowax 20M on Chromosorb P 45/60# column.

† GLC at 150° on a 5' 20% Apiezon L on Chromosorb P 60/80#

column.

Acid catalysed rearrangement of D-2,3-endo-epoxy-2-exo-phenylbornane (50)

m-Chloroperbenzoic acid (5 mg) was added to a soln of D-(-)-2-endo-phenylbornan-3-one (87; 20 mg) and D-2,3-endo-epoxy-2-exo-phenylbornane (50; 11 mg) in $CDCl_3$ (0.36 ml) and kept at 20° in an NMR tube. After 2 hr the NMR showed only the presence of D-(-)-2-endo-phenylbornan-3-one (87).

Spontaneous rearrangement of D-(+)-2,3-exo-epoxy-2-endo-phenylbornane (49)

Freshly prepared D-(+)-2,3-exo-epoxy-2-endo-phenylbornane (49; 1.00 g) was kept at 20° for 24 hr. NMR of a portion (30 mg) of the crude product showed the presence of 4-phenyl-2,2,3-trimethylcyclohex-3-en-1-al (119; 74%) and (-)-7-syn-hydroxy-1-phenylcamphene (68; 26%) with only a trace of any ketones (consistent with IR).

Adsorption of the balance of the crude product onto alumina and elution with n-pentane-benzene (9:1) and (3:1) gave 4-phenyl-2,2,3-trimethylcyclohex-3-en-1-al (119; 646 mg, 67%) as crystals (sublimation), m.p. 40-41°, n_D^{22} 1.5447, $[\alpha]_D^{22}$ ca. 0°(c 1.15), ν_{max} 2713, 1721, 755, 699 cm^{-1}; λ_{max} 233 nm (ϵ 5860)[78], NMR δ 9.98 ($J_{1\text{-}C\underline{H}O,1\text{-}H}$ 2.5 Hz; $C^1C\underline{H}O$); 7.26 ($W_{h/2}$ 6 Hz; C^4phenyl); 1.52 ($W_{h/2}$ 4 Hz; C^3Me); 1.30, 1.17 ppm (C^2gem-dimethyl): M^+ 228.152139 ($C_{16}H_{20}O$ requires 228.1511407),

(Found: C, 83.9; H, 8.6. $C_{16}H_{20}O$ requires: C, 84.2; H, 8.8%).

This aldehyde (119) readily underwent auto-oxidation to 4-phenyl-2,2,3-trimethyl-1-cyclohex-3-ene carboxylic acid (120) as crystals (triturated with n-pentane), m.p. 159-160°, $[\alpha]_D^{29}$ 0° (c 1.02), ν_{max} 2980 ($W_{h/2}$ 380 cm^{-1}), 1698, 760, 698 cm^{-1}; λ_{max} 231 nm (ϵ 4100)[78], NMR δ 9.97 ($W_{h/2}$ 15 Hz; C^1CO_2H); 7.33 ($W_{h/2}$ 6 Hz; C^4phenyl); 1.52 ($W_{h/2}$ 4 Hz; C^3Me); 1.30, 1.19 (C^2gem-dimethyl).

n-Pentane-benzene (1:1) eluted D-(-)-2-endo-phenylbornan-3-one (87; 21 mg, 2%) as crystals (n-pentane), m.p. and m.m.p. 95-96°, identical (IR, NMR, TLC) with an authentic sample.

Elution with benzene gave (-)-7-syn-hydroxy-1-phenyl-camphene (68; 237 mg, 24%) as crystals (n-pentane), m.p. and m.m.p. 66-68°, identical (IR, NMR, TLC) with an authentic sample.

Acid catalysed rearrangement of D-(+)-2,3-exo-epoxy-2-endo-phenylbornane (49)

m-Chloroperbenzoic acid (5 mg) was added to a soln of D-(+)-2,3-exo-epoxy-2-endo-phenylbornane (49; 31 mg) in $CDCl_3$ (0.36 ml) and kept at 20°in an NMR tube. After 1 hr the NMR showed the presence of 4-phenyl-2,2,3-trimethylcyclohex-3-en-1-al (119; 61%), (-)-7-syn-hydroxy-1-phenylcamphene (68; 8%), D-(-)-2-endo-phenylbornan-3-one (87; 23%) and D-(+)-2-exo-phenylbornan-3-one (88; 8%).

D-(+)-2-exo-phenylbornan-3-one (88; 31mg) under identical

conditions showed no sign of epimerisation to D-(-)-2-*endo*-phenylbornan-3-one (87) after 4 hr.

Thermal rearrangement of D-2-*exo*,3-*exo*-dihydroxy-2-*endo*-phenylbornane cyclic sulphites (95a and 95b)

(a). *anti*-D-(+)-2-*exo*,3-*exo*-dihydroxy-2-*endo*-phenylbornane cyclic sulphite (95a; 50 mg) was heated to 300° in an NMR tube for 30 min. The NMR tube was then allowed to cool, $CDCl_3$ (0.5 ml) added and the NMR recorded which showed the presence of only 4-phenyl-2,2,3-trimethylcyclohex-3-en-1-al (119) and D-(-)-2-*endo*-phenylbornan-3-one (87) in the ratio 2:1.

(b). As for (a). except a mixture of the cyclic sulphites (95a and 95b) consisting of 95a (43%) and 95b (57%) was rearranged. NMR showed the presence of only 4-phenyl-2,2,3-trimethylcyclohex-3-en-1-al (119) and D-(-)-2-*endo*-phenylbornan-3-one (87) in the ratio 3:1.

(c). As for (a). except D-(+)-2-exo-phenylbornan-3-one (88; 45mg) and *syn*-D-(+)-2-*exo*,3-*exo*-dihydroxy-2-*endo*-phenylbornane cyclic sulphite (95a; 5 mg) was rearranged. NMR showed only the presence of D-(-)-2-*endo*-phenylbornan-3-one (87) with a trace of 4-phenyl-2,2,3-trimethylcyclohex-3-en-1-al (119; *ca*. 4%).

(d). A mixture of the cyclic sulphites (95a and 95b) consisting of 95a (43%) and 95b (57%) was heated to 300° for 30 min to give a crude product (759 mg) which was adsorbed onto

activated alumina (50 g).

Elution with n-pentane gave a complex mixture of hydrocarbons (117 mg).

n-Pentane-benzene (3:1) eluted 4-phenyl-2,2,3-trimethylcyclohex-3-en-1-al (119; 429 mg, 72%) as crystals (sublimed), m.p. and m.m.p. 40-41°, identical (IR, NMR, TLC) with an authentic sample, which readily underwent auto-oxidation to 4-phenyl-2,2,3-trimethyl-1-cyclohex-3-ene carboxylic acid (120) as crystals (triturated with n-pentane), m.p. and m.m.p. 159-160°, identical (IR, NMR, TLC) with an authentic sample.

Elution with n-pentane-benzene (1:1) and benzene gave D-(-)-2-endo-phenylbornan-3-one (87; 145 mg, 24%) as crystals (n-pentane), m.p. and m.m.p. 95-96°, identical (IR, NMR, TLC) with an authentic sample.

Pyrolysis of 2,3-oxygenated butanes over glass or SE-30 coated glass

The compound to be pyrolysed was injected (3 ml/hr) into a heated (400°) glass tube (50 x 2.5 cm) packed with glass helices with a N_2 or SO_2 gas flow of 150 ml/min. The products were condensed in liquid air (for N_2 gas) or in ice-salt (for SO_2 gas) with near quantitative recovery. NMR showed the products present and their approximate yields. The quantitative yields (expressed as molar percentages) were determined by GLC at 50-150° on a 3' 20% Carbowax 20M on Chromosorb P 45/60# column. The reproduceability of a set of

results was determined by a number of replicate experiments and found to be within ca. -5% of the percentages quoted with the exception of the case where dioxolane formation was observed (see Table.5. p.63).

SE-30 coated glass was prepared by washing the helices and the tube with a soln of SE-30 (5 g) in CH_2Cl_2 (50 ml). After heating the tube up to the required temperature N_2 was passed through the system for 24 hr to remove any excess volatile materials.

The pyrolysis of compounds in the SE-30 coated glass tube were carried out as for the uncoated glass tube previously described.

The results obtained are summarised in Table.5. p.63.

D,L-amphi-4,5-Dimethyl-2-isopropyl-1,3-dioxolane (122) and meso-anti- and meso-syn-4,5-dimethyl-2-isopropyl-1,3-dioxolane (121a and 121b)

(a). aq. H_2SO_4 (50%, 0.2 ml) was added to a soln of the diol (113 or 115; 6.80 g) in isobutyraldehyde (6.80 g) and the mixture heated under reflux for 3 hr. Isolation by means of ether gave on distillation the dioxolane (122 or 121a and 121b).

D,L-Butan-2,3-diol (113) gave pure (GLC*, NMR) D,L-amphi-4,5-dimethyl-2-isopropyl-1,3-dioxolane (122; 3.99 g, 37%) b.p. 131-135°, n_D^{25} 1.4076, NMR (CCl_4) δ 4.60 ($J_{2\text{-}H,2\text{-}C\underline{H}Me_2}$ 4.4 Hz; C^2H); 3.41 ($W_{h/2}$ 12 Hz; C^4H and C^5H); 1.64 ($W_{h/2}$ 21 Hz; $C^2\text{-}C\underline{H}Me_2$); 1.27, 1.24, 1.19, 1.15, 1.09 (C^4Me and C^5Me); 0.88

ppm ($J_{2\text{-}C\underline{\underline{H}}Me_2,2\text{-}CH\underline{\underline{Me_2}}}$ 6.1 Hz; $C^2C\underline{\underline{HMe_2}}$).

meso-Butan-2,3-diol (115) gave pure (GLC*, NMR) meso-4,5-dimethyl-2-isopropyl-1,3-dioxolane (121; 3.62 g, 33%) consisting of a mixture of the anti-isomer (121a) and the syn-isomer (121b) in the ratio 1:2 as estimated by GLC and NMR, b.p. 134-138°, n_D^{25} 1.4136, NMR (CCl_4) δ 4.65 ($J_{2\text{-}H,2\text{-}C\underline{\underline{H}}Me_2}$ 4.8 Hz; C^2H of 121a)[119]; 4.39 ($J_{2\text{-}H,2\text{-}C\underline{\underline{H}}Me_2}$ 4.8 Hz; C^2H of 121b)[119]; 3.93 ($W_{h/2}$ 13 Hz; C^4H and C^5H); 1.60 ($W_{h/2}$ 26 Hz; $C^2\text{-}C\underline{\underline{H}}Me_2$); major signals at 1.09, 0.99 and minor signals at 1.06, 1.02 ($J^{app.}_{4\text{-}H,5\text{-}H}$ 4.4 Hz; C^4Me and C^5Me); 0.88 ($J_{2\text{-}C\underline{\underline{H}}Me_2,2\text{-}CH\underline{\underline{Me_2}}}$ 6.0 Hz; $C^2C\underline{\underline{HMe_2}}$ of 121b); 0.85 ppm ($J_{2\text{-}C\underline{\underline{H}}Me_2,2\text{-}CH\underline{\underline{Me_2}}}$ 6.1 Hz; $C^2C\underline{\underline{HMe_2}}$ of 121a).

(b). Pyrolysis of trans-2,3-epoxybutane (109; 1 g) with SO_2 over glass gave a crude product (981 mg) which showed the presence (NMR) of only the meso-syn-dioxolane (121b). Separation by preparative GLC† gave a mixture of the meso-anti- and meso-syn-dioxolanes (121a and 121b; 3:1) essentially identical (GLC*, NMR) with an authentic sample prepared as above.

(lit.[88]: 1-amphi-4,5-dimethyl-2-isopropyl-1,3-dioxolane b.p. 140°, n_D^{25} 1.4062).

* GLC at 150° on a 3' 20% Carbowax 20M on Chromosorb P 45/60 # column.

† GLC at 150° on a 5' 20% Carbowax 20M on Chromosorb P 45/60# column.

D,L- and meso-2,2,4,5-Tetramethyl-1,3-dioxolanes (124 and 123)

aq. H_2SO_4 (50%, 0.2 ml) was added to a soln of the diol (113 or 115; 6.80 g) in acetone (5.00 g) and the mixture heated under reflux for 3 hr. Isolation by means of ether gave on distillation the dioxolane (124 or 123).

D,L-Butan-2,3-diol (113) gave pure (GLC*, NMR) D,L-2,2,4,5-tetramethyl-1,3-dioxolane (124; 2.20 g, 22%) b.p. 109-112°, n_D^{25} 1.3953, NMR (CCl_4) δ 3.45 ($W_{h/2}$ 10.5 Hz; C^4H and C^5H); 1.28 (C^2gem-dimethyl); 1.19, 1.16, 1.15. 1.13. 1.11 ppm (C^4Me and C^5Me).

meso-Butan-2,3-diol (115) gave pure (GLC*, NMR) meso-2,2,4,5-tetramethyl-1,3-dioxolane (123; 2.11 g, 21%) b.p. 111-114°, n_D^{25} 1.4007, NMR (CCl_4) δ 3.98 ($W_{h/2}$ 10.5 Hz; C^4H and C^5H); 1.32 (C^2syn-Me)[120]; 1.22 (C^2anti-Me)[120]; major signals at 1.10, 1.00 and minor signals at 1.07, 1.01 ppm ($J^{app.}_{4\text{-}H,4\text{-}Me}$ and $J^{app.}_{5\text{-}H,5\text{-}Me}$ 4.8 Hz; C^4Me and C^5Me).

(lit.[88]: 1-2,2,4,5-tetramethyl-1,3-dioxolane b.p. 110°, n_D^{25} 1.3914).

* GLC at 150° on a 3' 20% Carbowax 20M on Chromosorb P 45/60# column.

D-(+)-Camphor benzene sulphonylhydrazone (134)

Concentrated hydrochloric acid (30 drops) was added to a

soln of D-(+)-camphor (43; 76.1 g) and benzene sulphonyl-hydrazide (86.1 g) in THF (250 ml) and the mixture heated under reflux for 6 hr. The THF was then distilled off and azeotropic distillation with benzene to a temperature of $80^{\circ}/760$ mm followed by vacuum distillation at 100° gave pure D-(+)-camphor benzene sulphonylhydrazone (134; 145 g, 95%) as crystals, m.p. 115-116°, $[\alpha]_D^{27}$ +14° (c 1.05), ν_{max} 3115, 1661, 1180, 1170, 752, 730, 688 cm^{-1}; λ_{max} 258 (shoulder, ϵ 1980), 266 (ϵ 1690), 273 nm (ϵ 1210): NMR δ 8.08-7.86 (ortho-H of benzene sulphonyl hydrazone); 7.65-7.43 (-NNHSO$_2$- (obscured) and meta- and para-H of benzene sulphonyl hydrazone); 0.90 ($C^{10}H_3$); 0.85 (C^9H_3); 0.49 ppm (C^8H_3).

LiMe

Li (16 g) was added to dry ether (400 ml) under an atmosphere of dry N_2. The mixture was then cooled to below -10° and MeBr (100g, 58 ml) in ether (200 ml) was added slowly with cooling over a period of 2 hr while the temperature was maintained at below -10° for the first 193 ml of soln. The last 65 ml of MeBr soln was added while the temperature was allowed to rise to between 10-20°. The reaction mixture was stirred for a further 2 hr and then filtered under an atmosphere of dry N_2 into a graduated separating funnel previously swept with dry N_2. From the reaction 590 ml of LiMe in ether (1.76 M) was obtained which corresponds to a yield of 99%.

D-(-)-Bornylene (77)[93]

LiMe in ether (305 ml, 1.76 M) was added over 40 min to crude D-(+)-camphor benzene sulphonyl hydrazone (76.5 g) in ether (100 ml) under an atmosphere of dry N_2 at 20°. The reaction was stirred for a further 150 min until the evolution of N_2 ceased. Addition of H_2O and isolation by means of n-pentane followed by fractional distillation through a column packed with glass helices, filtration through 1 Kg of activated alumina and removal of solvent *via* fractional distillation afforded crude D-(-)-bornylene (77).

Distillation then gave D-(-)-bornylene (77; 16.0 g, 47%) as volatile crystals, m.p. 109-110°, $[\alpha]_D^{28}$ -19° (toluene; c 1.12), ν_{max} 718 cm^{-1}, NMR δ 5.92 ($J_{2\text{-}H,3\text{-}H}$ 5.8, $J_{3\text{-}H,4\text{-}H}$ 2.9 Hz; C^3H); 5.66 ($J_{2\text{-}H,3\text{-}H}$ 5.8, $J_{2\text{-}H,6\text{-}exo\text{-}H}$ 0.9 Hz; C^2H); 2.28 ($J_{3\text{-}H,4\text{-}H}$ 2.9 Hz; C^4H); 1.03 ($C^{10}H_3$); 0.83 (C^9H_3); 0.77 (C^8H_3).

(lit.[94]: L-(+)-bornylene m.p. 113°; D-(-)-bornylene $[\alpha]_D$ -19.3° (toluene)).

1,1-Diphenylethan-1-ol-2-yl mercury acetate (127)

$Hg(OAc)_2$ (3.19 g) was added to a soln of 1,1-diphenylethylene (126; 1.8 g) in aq. THF (1:1; 20 ml) and the mixture stirred at 20° for 24 hr. Isolation of the crude product by means of ether gave a mixture (3.61 g) consisting of (NMR), 1,1-diphenylethylene (126; 360 mg, 20%) and 1,1-diphenylethan-1-ol-2-yl mercury acetate (127; 3.25 g, 71%). The presence of

1,1-diphenylethylene (126) was confirmed by GLC*.

The hydroxyalkyl mercury acetate (127) was isolated pure by crystallization (3.10 g) as an amorphous solid (CH_2Cl_2-ether), m.p. 116.5-117.5°, ν_{max} (KBr) 3370 (broad), 1582, 753, 698 cm^{-1}; λ_{max} 250 (ϵ 1020), 254 (ϵ 1080), 260 (ϵ 1050), 266 (inflexion, ϵ 793), 270 (inflexion, ϵ 564): NMR δ 7.27 ($W_{h/2}$ 16 Hz; C^1gem-diphenyl); 3.76 ($W_{h/2}$ 13 Hz; C^1OH); 2.85 ($J_{2\text{-}H,^{199}Hg}$ 204.4 Hz; C^2H_2); 1.84 ppm (C^2HgOAc): (Found: C, 43.0; H, 3.5. $C_{16}H_{16}HgO_3$ requires: C, 42.1; H, 3.5%).

The hydroxyalkyl mercury acetate (127; 200 mg) was dissolved in CH_2Cl_2 and shaken with aq. $NaCl^{42}$. Isolation by means of CH_2Cl_2 gave 1,1-diphenylethan-1-ol-2-yl mercury chloride (128; 187 mg, 99%) as an amorphous solid (CH_2Cl_2), m.p. 142-143.5 (decomp.), ν_{max} (KBr) 3478 (sharp), 750, 695 cm^{-1}; λ_{max} 250 (shoulder, ϵ 800), 254 (ϵ 853), 260 (ϵ 857), 266 (inflexion, ϵ 677), 270 (inflexion, ϵ 488): NMR δ 7.27 ($W_{h/2}$ 4.5 Hz; C^1gem-diphenyl); 2.93 ($J_{2\text{-}H,^{199}Hg}$ 194.4 Hz; C^2H_2); 2.63 ppm ($W_{h/2}$ 8 Hz; C^1OH): M^+ (for ^{202}Hg, ^{35}Cl) 434.035727 ($C_{14}H_{13}ClHgO$ requires 434.036113).

* GLC at 80° on a 5' 5% FFAP on aeropak 30 80/100# column.

NaBH$_4$ reduction of 1,1-diphenylethan-1-ol-2-yl mercury acetate (127)

A soln (0.5 M) of $NaBH_4$ in aq. NaOH (20 ml, 3 M) was added to a soln of the hydroxyalkyl mercury acetate (127; 1 g) in THF (10 ml) and aq. NaOH (10 ml, 3 M) and the mixture

stirred at 20° for 24 hr. Isolation by means of ether gave 1,1-diphenylethan-1-ol (129; 433 mg, 100%), m.p. and m.m.p. 80-81°, ν_{max} 3602, 698 cm^{-1}; λ_{max} 246 (shoulder, ϵ 161), 249 (shoulder, ϵ 227), 253 (ϵ 318), 259 (ϵ 385), 265 (ϵ 371), 268 (shoulder, ϵ 192): NMR δ 7.37 ($W_{h/2}$ 5 Hz; C^1gem-diphenyl); 2.19 (C^1OH); 1.93 ppm (C^2H_3).

(lit.[121]: m.p. 81°, ν_{max} 3623 cm^{-1}, λ_{max} 252.5 (ϵ 430), 258.1 (ϵ 494), 264.0 (ϵ 380): NMR δ 7.22 (C^1gem-diphenyl); 1.85 ppm (C^2H_3)).

Oxymercuration-demercuration of camphene (130)[39]

$Hg(OAc)_2$ (30.0 g) was added to a soln of camphene (130; $[\alpha]_D^{20}$ +17° (c 1.02); 10 g) in aq. THF (1:1; 100 ml) and the mixture stirred at 20° for 5 hr. aq. NaOH (3 M; 100 ml) was added followed by a soln (0.5 M) of $NaBH_4$ in aq. NaOH (3 M; 100 ml) and stirring continued at 20° for 30 min. Isolation by means of ether gave a solid (12.1 g). This material was treated as follows:

(a). Adsorption of the crude product (5.81 g) onto 5% deactivated alumina (300 g) and elution with n-pentane gave a mixture of four isomeric divinylmercurys (133; 269 mg, 9%) as crystals (acetone), m.p. 117-118°, $[\alpha]_D^{25}$ +6° (c 1.06), ν_{max} 2876, 2862, 1300, 1255, 1197, 1102, 1053, 953, 819, 804, 761, 698 cm^{-1}; λ_{max} 237 nm (ϵ 15400), NMR δ 6.26 ($W_{h/2}$ 2.5 Hz); 5.78, 5.50 (integral ratio respectively 15:6:2; olefinic

protons); 2.62 ($W_{h/2}$ 6.5 Hz; C^1H); 1.25, 1.18 ppm (C^3gem-dimethyl): M^+ (for ^{202}Hg) 472.204286 ($C_{20}H_{30}Hg$ requires 472.205365).

Elution with benzene gave camphene hydrate (131; 2.44 g) m.p. amd m.m.p. 150-151°, $[\alpha]_D^{28}$ -5° (c 1.06), ν_{max} 3608 cm^{-1}, NMR δ 1.37 ($C^{2-exo-}OH$), 1.17 (C^2H_3), 0.99 ($C^{3-exo-}Me$), 0.90 ppm ($C^{3-endo-}Me$).

(lit.[94] : camphene hydrate m.p. 150-151°).

(b). The crude product (3.86 g) was heated in a sublimation apparatus at 100° and 0.1 mm pressure for 8 hr. The residue (1.89 g) on crystallization from n-pentane gave di-(2-exo-hydroxycamphanyl)-mercury (132; 209 mg) m.p. 166-167° (decomp.), $[\alpha]_D^{25}$ -20° (c 1.01), ν_{max} 3360 cm^{-1} (very broad), NMR δ 1.92 ($C^{2-exo-}OH$); 1.29 ($-CH_2HgCH_2-$); 1.00 ($C^{3-exo-}Me$); 0.92 ppm ($C^{3-endo-}Me$): M^+ (for ^{202}Hg) 508.227186 ($C_{20}H_{34}HgO_2$ requires 508.226491).

LAH reduction of di-(2-exo-hydroxycamphanyl)-mercury (132)

LAH (100 g) was added to a soln of the dialkylmercury (132; 50 mg) in ether (5 ml) and the mixture heated under reflux for 1 hr. Decomposition of excess LAH by addition of $Na_2SO_4.10H_2O$ followed by H_2O, filtration and removal of solvent gave camphene hydrate (131; 17 mg, 56%) identical with an authentic sample (IR, GLC*, NMR)

* GLC at 45° on a 5' 3% FFAP on Chromosorb P 60/80# column.

Oxymercuration-demercuration of D-(-)-bornylene (77)

$Hg(OAc)_2$ (7.05 g) was added to a soln of the olefin (77; $[\alpha]_D^{28}$ -19° (toluene; c 1.12); 3 g) in aq. THF (1:1; 45 ml) and the mixture stirred at 20° for 150 min. A sample, isolated by means of ether, gave an NMR spectrum which did not exhibit signals characteristic of olefinic protons. aq. NaOH (3 M; 12 ml) was added, followed by a soln (0.5 M) of $NaBH_4$ in aq. NaOH (3 M; 12 ml) and the mixture stirred at 20° for 20 min. Isolation of the terpenoid material by means of ether gave a semi-solid product (3.01 g).

Adsorption of this material (1.85 g) onto 10% deactivated alumina (100 g) and elution with n-pentane gave a mixture (GLC*, NMR) of isobornyl acetate (136) and epiisobornyl acetate (138).

Isobornyl acetate (136) prepared from isoborneol (135) gave the following NMR spectrum δ 4.68 ($J^{app.}_{2\text{-}\underline{exo}\text{-}H,3\text{-}\underline{endo}\text{-}H}$ 5.7, $J^{app.}_{2\text{-}\underline{endo}\text{-}H,3\text{-}exo\text{-}H}$ 5.7Hz; $C^{2\text{-}\underline{endo}\text{-}}H$); 2.00 ($C^{2\text{-}\underline{exo}\text{-}}OAc$); 0.98 ($C^9H_3$); 0.84 ppm ($C^8H_3$ and $C^{10}H_3$)[101]. Subtraction of the NMR spectrum of isobornyl acetate (136) from that of the mixture gave a spectrum consistent with the epiisobornyl acetate structure (138) NMR δ 4.49 ($J^{app.}_{2\text{-}\underline{endo}\text{-}H,3\text{-}\underline{endo}\text{-}H}$ 6.8, $J^{app.}_{2\text{-}\underline{exo}\text{-}H,3\text{-}\underline{endo}\text{-}H}$ 4.9 Hz; $C^{3\text{-}\underline{endo}\text{-}}H$); 1.98 ($C^{3\text{-}\underline{exo}\text{-}}OAc$); 1.02 ($C^8H_3$); 0.90 ($C^{10}H_3$); 0.88 ppm ($C^9H_3$). The identity of these products was confirmed by LAH reduction of the mixture to give isoborneol (135) and epiisoborneol (137) in the same ratio (GLC , NMR) as that of isobornyl acetate (136) and epiisobornyl

acetate (138).

Elution with n-pentane-benzene (19:1) gave isoborneol (135; 261 mg) as crystals (sublimation), m.p. and m.m.p. 207-208°, $[\alpha]_D^{20}$ -19° (toluene, c 1.02), ν_{max} 3616 cm^{-1}, NMR δ 3.62 ($J^{app.}_{2\text{-}\underline{endo}\text{-}H,3\text{-}\underline{endo}\text{-}H}$ 6.7, $J^{app.}_{2\text{-}\underline{endo}\text{-}H,3\text{-}\underline{exo}\text{-}H}$ 4.2 Hz; $C^{2\text{-}\underline{endo}\text{-}}H$); 1.02 ($C^8H_3$); 0.90 ($C^{10}H_3$); 0.82 ppm ($C^9H_3$).

(lit.[94] : isoborneol (135) m.p. 212° corr. (closed tube), $[\alpha]_D$ -21° (toluene)).

Continued elution with n-pentane-benzene (19:1), (9:1) and (3:1) gave a mixture of isoborneol (135; 343 mg) and epiisoborneol (137; 188 mg) as estimated by GLC*.

Further elution with n-pentane-benzene (3:1) gave epiisoborneol (137; 89 mg) as crystals (sublimation), m.p. 190-191°, $[\alpha]_D^{28}$ +12° (toluene, c 1.02), ν_{max} 3613 cm^{-1}, NMR δ 3.83 ($J^{app.}_{2\text{-}\underline{endo}\text{-}H,3\text{-}\underline{endo}\text{-}H}$ 6.8, $J^{app.}_{2\text{-}\underline{exo}\text{-}H,3\text{-}\underline{endo}\text{-}H}$ 4.9 Hz; $C^{3\text{-}\underline{endo}\text{-}}H$); 1.35 ($C^{3\text{-}\underline{exo}\text{-}}OH$); 1.08 ($C^8H_3$); 0.88 ($C^{10}H_3$); 0.83 ppm ($C^9H_3$).

(lit.[94] : epiisoborneol (137) m.p. 194.5°, $[\alpha]_D^{30}$ +13.2° (toluene)).

The product composition of the mixture was estimated by GLC* as isobornyl acetate (136; 456 mg, 10%), epiisobornyl acetate (138; 424 mg, 9%), isoborneol (135; 1.21 g, 36%) and epiisoborneol (137; 920 mg, 27%).

* GLC at 120° on a 5' 5% FFAP on Aeropak 30 80/100# column.

LAH reduction of the isobornyl acetate (136) and epiisobornyl acetate (138) mixture derived from oxymercuration-demercuration of D-(-)-bornylene (77)

LAH (102 mg) was added to a soln of the acetate (136 and 138; 10:9; 49 mg) in ether (5 ml) and the mixture heated under reflux for 4 hr. Decomposition of excess LAH by addition of $Na_2SO_4.10H_2O$ followed by H_2O, filtration and removal of solvent gave a mixture of isoborneol and epiisoborneol (135 and 137; 10:9; 32 mg, 90%) by GLC* and NMR.

* GLC at 120° on a 5' 5% FFAP on Aeropak 30 80/100# column.

Isobornyl acetate (136)

Ac_2O (20 ml) was added to a soln of isoborneol (135; $[\alpha]_D^{28}$ -1° (c 1.08); 2.51 g) in pyridine (100 ml) and stirred at 20° for 27 hr. Isolation by means of ether and distillation of the crude product in a micro-distillation apparatus gave isobornyl acetate (136; 1.63 g, 51%) as an oil, b.p.$_{8\ mm}$ 95°, n_D^{24} 1.4633, $[\alpha]_D^{28}$ -2° (c 1.00), ν_{max} 1730, 1243 cm^{-1}: NMR δ 4.68 ($J^{app.}_{2\text{-}\underline{exo}\text{-}H,3\text{-}\underline{endo}\text{-}H}$ 5.7, $J^{app.}_{2\text{-}\underline{endo}\text{-}H,3\text{-}\underline{exo}\text{-}H}$ 5.7 Hz; $C^{2\text{-}\underline{endo}\text{-}}H$); 2.00 ($C^{2\text{-}\underline{exo}\text{-}}OAc$); 0.98 ($C^8H_3$); 0.84 ppm ($C^9H_3$ and $C^{10}H_3$).

(lit.[94] : D,L-isobornyl acetate (136) b.p.$_{40\ mm}$ 131.8°, n_D^{20} 1.4639).

Oxymercuration of β-pinene (139)

$Hg(OAc)_2$ (31.9 g) was added to a soln of β-pinene (139;

$[\alpha]_D^{28}$ -15° (c 1.15); > 98% by GLC*; 13.6 g) in aq. THF (1:1; 200 ml) and the mixture stirred at 20° for 10 min. Isolation by means of ether and washing (15 times) with H_2O gave the olefin mercury acetate (140 and 142; 7:2 (NMR); 20.2 g, 51%) as a waxy solid, $[\alpha]_D^{30}$ -14° (c 1.01), ν_{max} (smear) 1603, (CS_2) 2821, 1302, 798 cm^{-1}; λ_{max} 203 (ϵ 9390), 245 nm (ϵ 8130): NMR δ 5.33, 4.99 (C^3H and $C^{10}H$ olefinic protons in 140 and 142 respectively; 7:2); 2.75 ($-C\underline{H}_2HgOAc$ in 140); 2.01 (-HgOAc); 1.29 (C^8H_3)[27]; 0.89 ppm (C^9H_3).

The alkenylmercury acetates (140 and 142; 7.79 g) was dissolved in CH_2Cl_2 and shaken with aq. NaCl[42]. Isolation by means of CH_2Cl_2 gave the mixed alkenylmercury chlorides (141 and 143; 7:2 (NMR); 187 mg, 99%) as needles, m.p. 87-89°, $[\alpha]_D^{30}$ -24° (c 1.09), ν_{max} 2836, 805 cm^{-1}; λ_{max} 203 (ϵ 9210), 249 nm (ϵ 8240): NMR δ 5.32, 4.89 (C^3H and $C^{10}H_3$ olefinic protons in 141 and 143 respectively; 7:2); 2.76 ($-C\underline{H}_2HgCl$); 1.30 (C^8H_3); 0.89 ppm (C^9H_3): M^+ (for ^{202}Hg, ^{35}Cl) 372.056848 ($C_{10}H_{15}ClHg$ requires 372.056182).

Both the alkenylmercury acetates and chlorides decompose rapidly on keeping.

* GLC at 50° on a 5' 5% FFAP on Aeropak 30 80/100# column.

Demercuration of the alkenylmercury acetates (140 and 142)

The alkenylmercury acetates (140 and 142) prepared as from β-pinene (3.40 g) were reduced *in situ* by the addition of aq. NaOH (3 M; 25 ml) followed by a soln (0.5 M) of $NaBH_4$ in

aq. NaOH (3 M; 25 ml) and stirring at 20° for 10 min. Isolation by means of ether gave the crude product (3.31 g) which contained only a trace of alcohols (IR). The crude terpenoid material contained β-pinene (139; ca.385 mg, 11%) and dimeric compounds (144; 1.96 g, 58%) along with traces of other terpenoid compounds (ca. 965 mg) as estimated by GLC*. The dimeric compounds with very similar R_f values were eluted by GLC*. The integral percentages of the four peaks due to dimeric compounds (144) were ca. 76, 10, 8 and 6% in order of decreasing Rf values.

The major dimeric compound by analytical GLC†, was isolated by preparative GLC , as an oil, n_D^{22} 1.5111, $[\alpha]_D^{30}$ -19° (c 1.08), ν_{max} 2835 cm^{-1}, λ_{max} 215 nm (ε 10900), NMR δ 5.20, 4.52 olefinic protons, ca. 2:1 respectively); major signals at 1.27 and 0.83 (C^8H_3 and C^9H_3); minor signals at 1.24, 1.22, 1.08, 0.87, 0.75 ppm: M^+ 270.236203 ($C_{20}H_{30}$ requires 270.234740), (Found: C, 88.9; H, 11.3. $C_{20}H_{30}$ requires: C, 88.8, H, 11.2%).

* GLC at 150° on a 5' 5% FFAP on Aeropak 30 80/100# column

† GLC from 50 to 100° on a 5' 5% FFAP on Aeropak 30 80/100# column.

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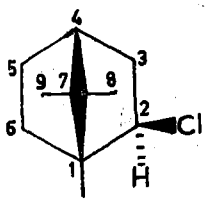
Acknowledgement is made to Ivon Watkins-Dow Ltd. for financial support.



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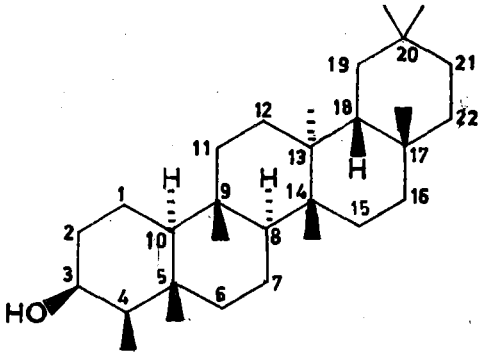

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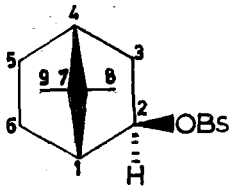

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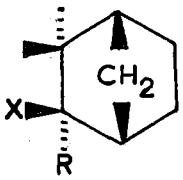

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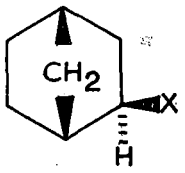
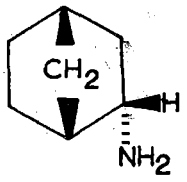
(5) X,Cl; R, Me



(6) X,OBs
(7) X,Cl
(8) X, NH_2



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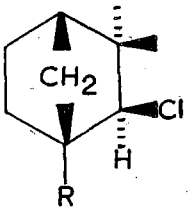

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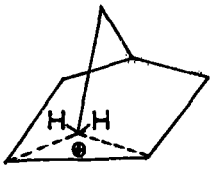

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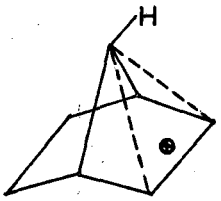

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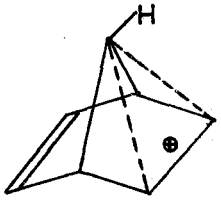

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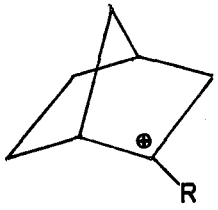
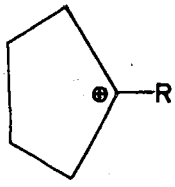


(14) R,Me
(15) R,φ



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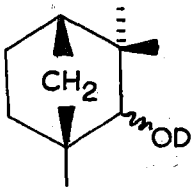
(17) R,φ



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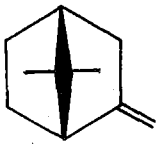

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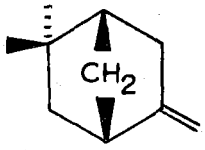

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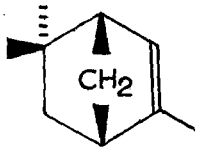

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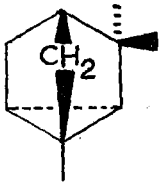

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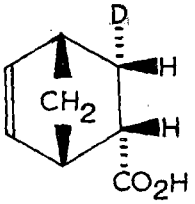

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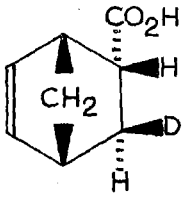

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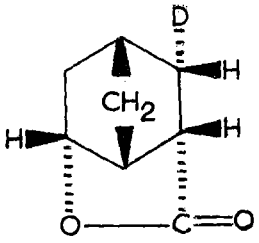

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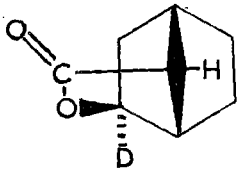

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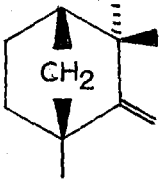

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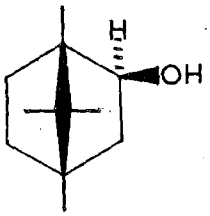

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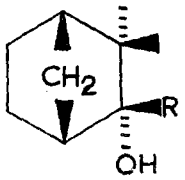
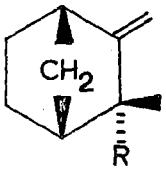


(29) R, p-anisyl
optically active



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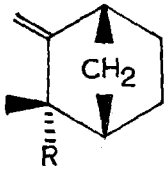

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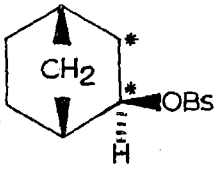

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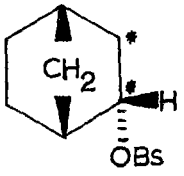

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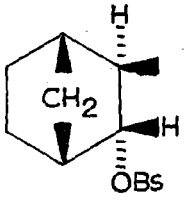

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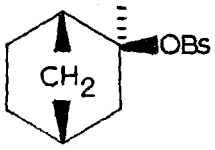

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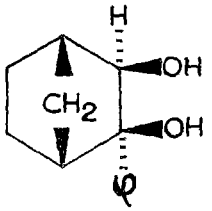

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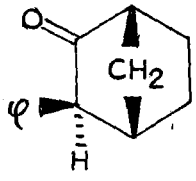

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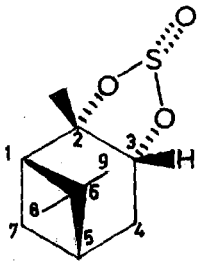

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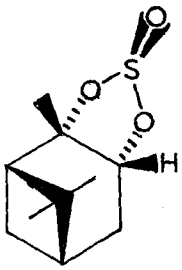

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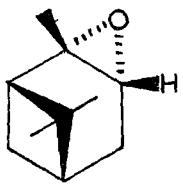

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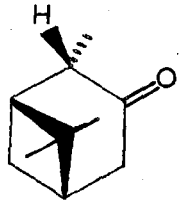

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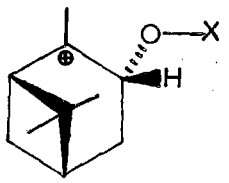
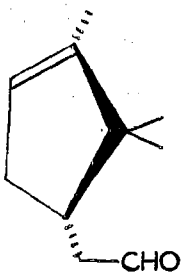


(41a) X, $MgCl_2^{\ominus}$
(41b) X, $SO_2^{\ominus}$



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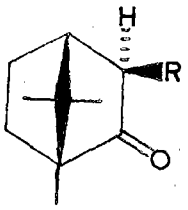
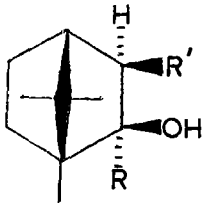
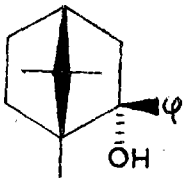


(43) R,H
(44) R,D



(45) R,Me; R′,H
(46) R,φ ; R′,H
(47) R,φ ; R′,D



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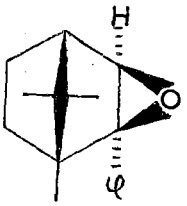

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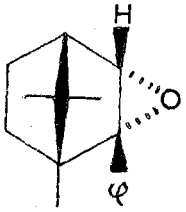

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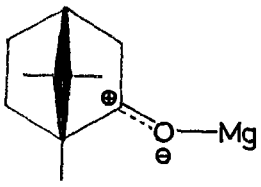

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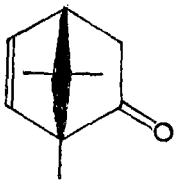

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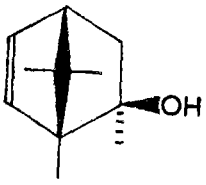

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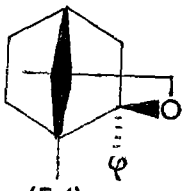

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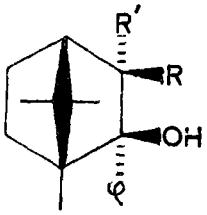
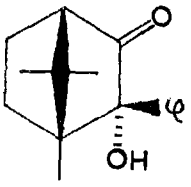
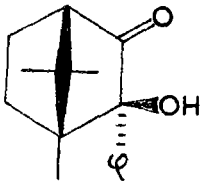


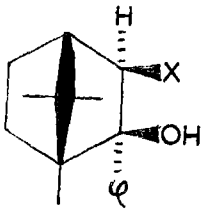
(55) R,R′=O
(56) R,R′ $\begin{matrix}-S\\-S\end{matrix}$



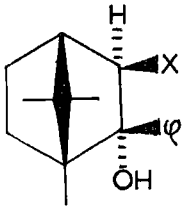
(57)



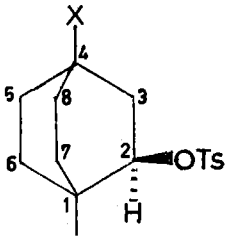
(58)



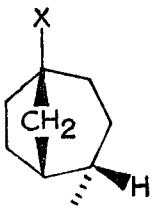
(59) X,OH
(60) X,OTs



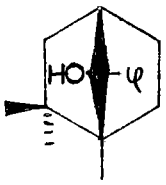
(61) X,OH
(62) X,OTs



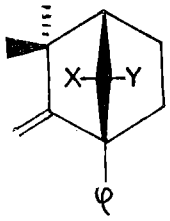
(63)



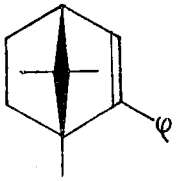
(64)



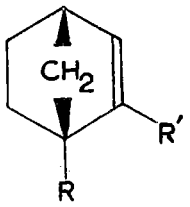
(65)



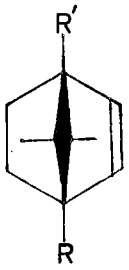
(66) X,H; Y,H
(67) X,D; Y,H
(68) X,OH; Y,H
(69) X,H; Y,OH
(70) X,H; Y,Br
(71) X,Y=O



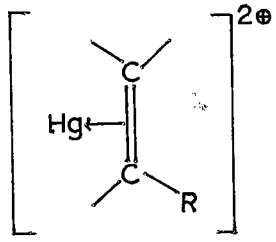
(72)



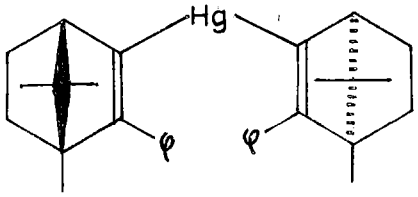
(73) R,H; R′,H
(74) R,Me; R′,H
(75) R,H; R′,Me



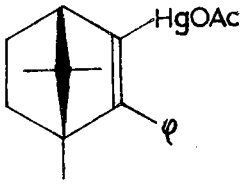
(76) R,H; R′,H
(77) R,Me; R′,H
(78) R,Me; R′,Me



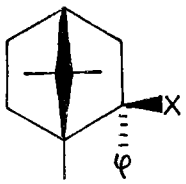
(79)



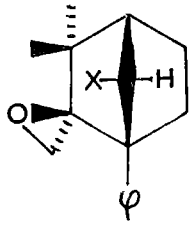
(80)



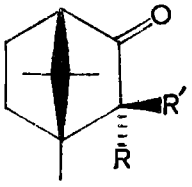
(81)



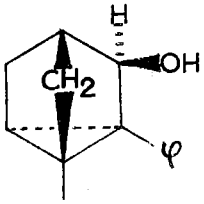
(82) X,O$^{\ominus}$Na$^{\oplus}$
(83) X,O—CS—S$^{\ominus}$Na$^{\oplus}$
(84) X,O—CS—SEt



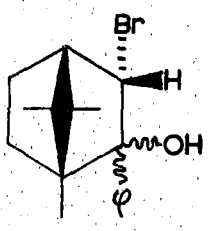
(85) X,H
(86) X,OH



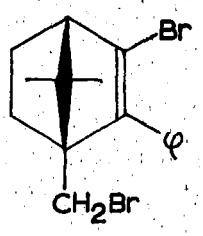
(87) R,φ ; R′,H
(88) R, H; R′,φ



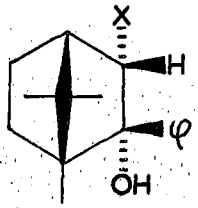
(89)



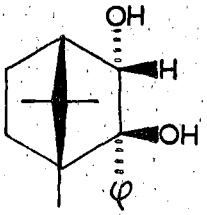
(90)



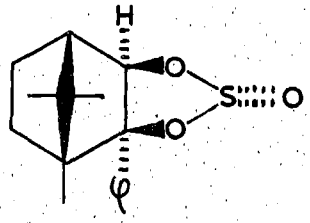
(91)



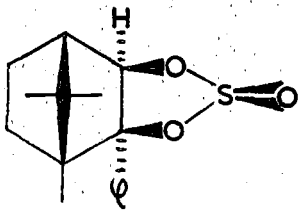
(92) X,OH
(93) X,OTs



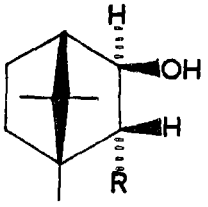
(94)



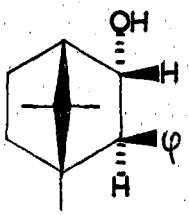
(95a)



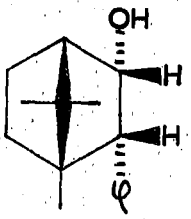
(95b)



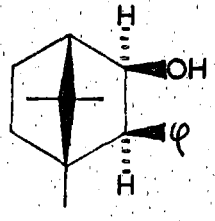
(96) R, φ
(97) R, cyclohex-1'-en-1'-yl



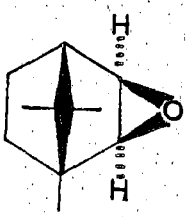
(98)



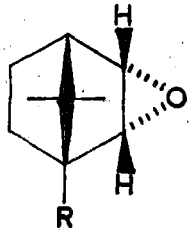
(99)



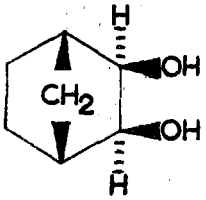
(100)



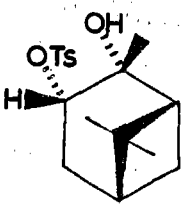
(101)



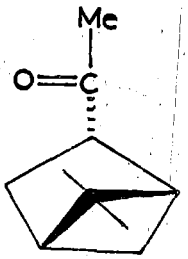
(102) R,H
(103) R,Me



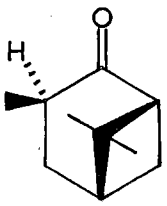
(104)



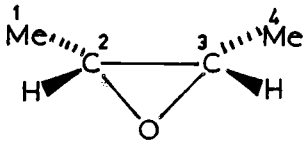
(105)



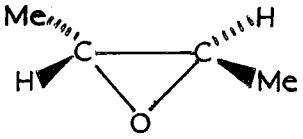
(106)



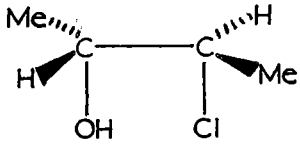
(107)



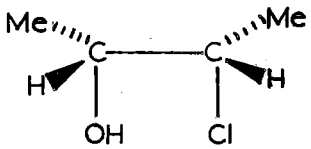
(108)



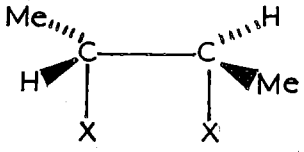
(109)



(110)

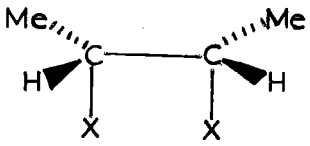


(111)



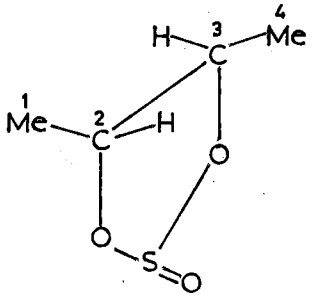
(112) X,Cl

(113) X,OH

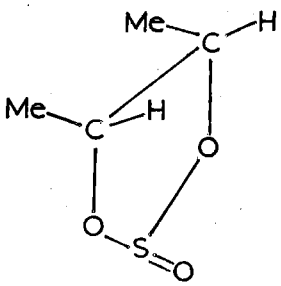


(114) X,Cl

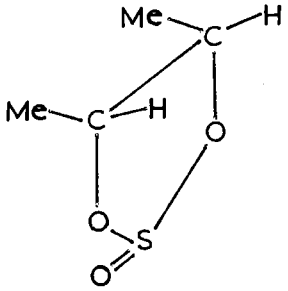
(115) X,OH



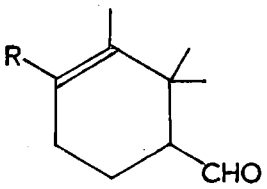
(116)



(117a)

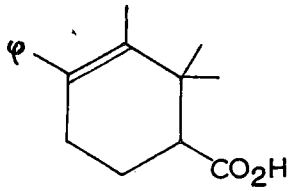


(117b)

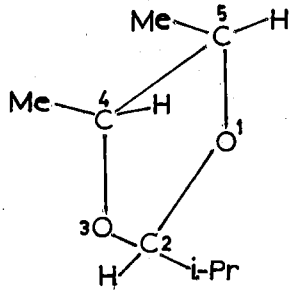


(118) R,H

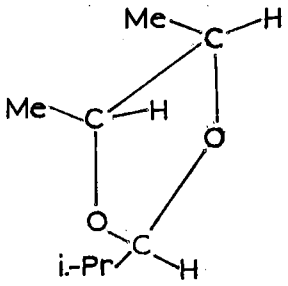
(119) R,φ



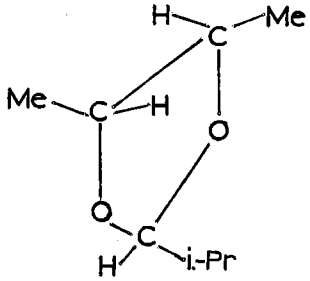
(120)



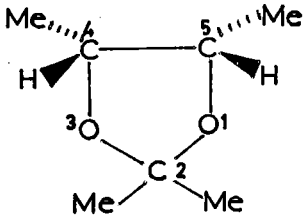
(121a)



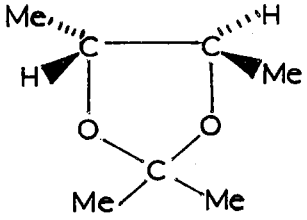
(121b)



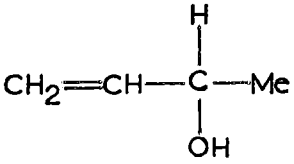
(122)



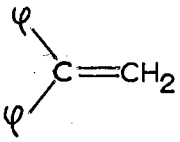
(123)



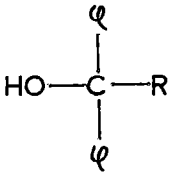
(124)



(125)



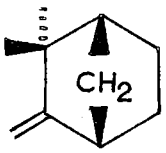
(126)



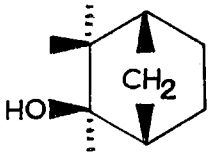
(127) R, $-CH_2-HgOAc$

(128) R, $-CH_2-HgCl$

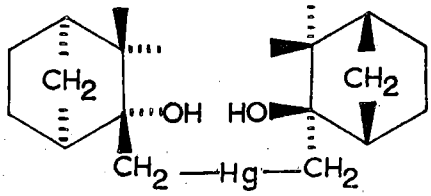
(129) R, Me



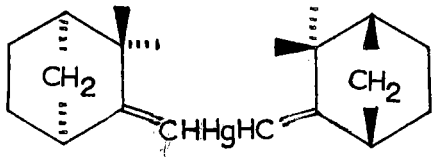
(130)



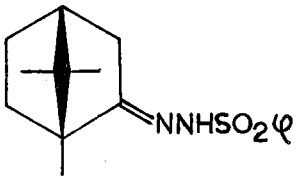
(131)



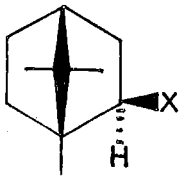
(132)



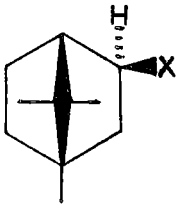
(133)



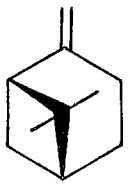
(134)



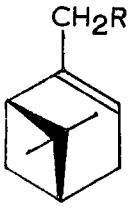
(135) X,OH
(136) X,OAc



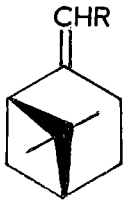
(137) X,OH
(138) X,OAc



(139)



(140) R,-HgOAc
(141) R,-HgCl



(142) R,-HgOAc
(143) R,-HgCl

$C_{10}H_{15}—C_{10}H_{15}$

(144)